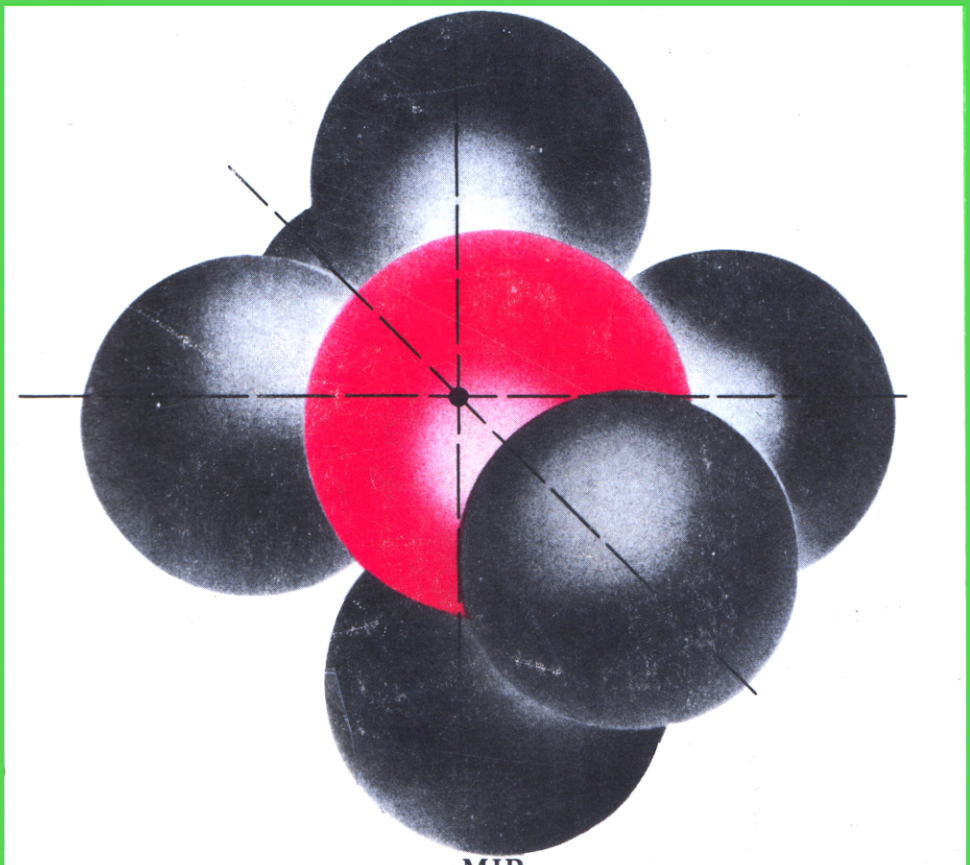
FUNDAMENTALS OF ORGANIC CHEMISTRY

A.N. NESMEYANOV, N.A. NESMEYANOV



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ИЗДАТЕЛЬСТВО МИР

FUNDAMENTALS OF ORGANIC CHEMISTRY

by
A.N. Nesmeyanov
and
N.A. Nesmeyanov

This book is Volume I of the four-volume textbook intended for a systematic study of organic chemistry. The material is divided into two parts and covers a considerably wider field than the normal university treatment of the subject. Part One (the first three volumes) is constructed on "classical" lines. Part Two (volume IV) is intended for attentive reading rather than for close study.

Volume I comprises the following sections — introduction, aliphatic (saturated and unsaturated) compounds. The material is presented in order of increasing sophistication — first, rather simply and in detail, and then in more and more concise form.

This book has been translated from the second revised Russian edition published in two volumes in 1974. The first Russian edition (in two volumes) was published in 1969.

This book may be used for self-study and for reading the course of organic chemistry at universities and chemical higher schools. It will undoubtedly be of interest to post-graduates, teachers and young scientists and engineers working in the field of organic chemistry.

FUNDAMENTALS OF ORGANIC CHEMISTRY

Volume I

А. Н. Несмеянов, Н. А. Несмеянов

НАЧАЛА ОРГАНИЧЕСКОЙ ХИМИИ

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Brief Contents
of Volumes I-IV

Part One

Volume I

Introduction
Acyclic Compounds
Saturated Compounds
Unsaturated Compounds

Volume II

Acyclic Compounds
Heterofunctional Compounds
Alicyclic Compounds
Alicyclic Hydrocarbons and Their Derivatives

Volume III

Aromatic Compounds
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Polyhydric Aromatic Compounds
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Part Two

Volume IV

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Carbanions
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Proteins
Nucleotides and Polynucleotides. Protein Biosynthesis
Enzymes

Preface

The present course of organic chemistry is intended for chemical departments at universities and higher schools of chemistry. It has evolved from the lectures read by one of the authors to students of chemistry at Moscow State University and includes the elements of theoretical foundations of organic chemistry—the subject matter of the course taught at Moscow State University by Academician O. A. Reutov and the co-author of this book. This accounts for the order of presentation of the material, which is more classical and departs somewhat from that adopted in many modern textbooks, chiefly those written by Nenitzescu, Roberts and Caserio, Cram and Hammond. This traditional approach consists in presenting first an introduction (with a brief historical outline of organic chemistry and of development of the fundamental concepts, methods of characterization of organic compounds, analysis, determination of molecular formulas, structural theory), followed by a systematic exposition of the material in the sequence: the aliphatic series, alicyclic compounds, the aromatic series, heterocyclic compounds. These topics constitute the subject matter of Part I (volumes I, II, and III).

The theoretical material—elements of the theory of chemical reactions, the chemical-bond theory, classical and dynamic stereochemistry, conformations—will be found incorporated, as separate sections, in the appropriate places in the text, after the adequate factual material has accumulated for assimilation of the theory introduced. The same applies to the physical methods of investigation of organic compounds. From our own experience, we know that this approach makes it possible to pass gradually to the most advanced topics of organic chemistry.

Part I, which consists of three volumes, is intended for close study. Part II (volume IV) is written in a more condensed form and is therefore difficult for understanding. The material introduced in Part II partly generalizes and extends the concepts associated with reaction mechanisms, which are treated at a more elementary level in Part I.

It contains chapters dealing with carbanions, free radicals, carbenes, carbonium ions, rearrangements, elimination reactions, the transition state. Furthermore, Part II includes more sophisticated material of organic chemistry, such as organoelement compounds, nonbenzoid aromatics, isoprenoids (including terpenes and steroids), alkaloids, proteins, enzymes, nucleic acids. Preliminary information on organoelement compounds, isoprenoids, alkaloids, and proteins is given in Part I.

We think that all the topics covered by Part II must be read attentively in order to get a general picture; chemistry students need not study them. Teaching experience shows that the mastering of this material is a rather formidable task in a general course. Chemistry majors will be able to master this material in the later years of their study.

Thus, the amount of material that the student is strongly urged to work through in detail is not too large, the more so that we allowed for some repetitions (each time in a more extended form), which will undoubtedly facilitate the study.

Both authors have equally contributed to all the principal sections of all the four volumes. This book could not have been written without the help of our friends and colleagues, to whom we express our deep gratitude for the various contributions to the text. We very much appreciate the contributions made by Professor D. A. Bochvar, who has written the section devoted to the modern theory of the chemical bond, and by Professor A. I. Kitaigorodsky who has written the section on diffraction methods of structural analysis.

The authors are greatly indebted to Academicians M. I. Kabachnik, V. A. Engelgardt, and A. E. Braunshtein, Associate Member of the USSR Academy of Sciences N. K. Kochetkov, Professors M. M. Botvinnik and Z. A. Shabarova, Doctors V. T. Aleksanyan and E. I. Fedin for the perusal of separate sections of the manuscript and for their valuable corrections and many critical comments and suggestions for its improvement.

We also wish to pay tribute to Academician M. M. Shemyakin, Professor N. S. Wulfson, Associate Member N. K. Kochetkov, Associate Professors Yu. A. Arbuzov and Yu. A. Ustynyuk who provided us with some data for inclusion in the book. Finally, we wish to emphasize that in acknowledging the kind assistance of our colleagues and friends, we relieve them of all responsibility for any flaws, omissions, or errors in this book.

We extend our heartfelt thanks to M. A. Vinogradova, E. I. Kan and V. A. Ventskovskaya for the indispensable assistance in preparing the manuscript for publication.

We will be grateful for any constructive criticism of this book.

A. N. Nesmeyanov, N. A. Nesmeyanov

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PART ONE

Chapter 1

Introduction

1.1. The Subject of Organic Chemistry. The Historical Background

Chemistry is concerned mainly with study of chemical entities—chemical compounds—and their transformations. An independent branch of the chemical science—*organic chemistry*—deals with compounds formed by carbon with other elements. Carbon forms an especially large number of compounds with elements called **organogenetic elements** or **organogens**: hydrogen (H), oxygen (O), nitrogen (N), sulphur (S), phosphorus (P), and the halogens. These compounds are widespread in nature and have mostly been investigated and produced artificially through synthesis.

Some organic compounds have been known to man in a more or less pure form since times immemorial (for example, vinegar—an aqueous solution of acetic acid, and many organic dyes). A number of organic compounds, such as urea and ethyl ether (sulphuric ether), were produced by alchemists. A great many compounds, especially organic acids (oxalic, citric, lactic, and others) and organic bases (alkaloids), were isolated from plant and animal sources in the second half of the eighteenth and at the beginning of the nineteenth century. This period should be regarded as the birth of scientific organic chemistry corresponding to the two branches of the former chemistry which was separated into mineral chemistry and the chemistry of plants and animals (the name "organic chemistry" originated later).

In the eighteenth century and in the first quarter of the nineteenth century there reigned the belief that the chemistry of living matter was fundamentally different from the chemistry of inanimate matter (mineral chemistry) and that living organisms built their substances under the influence of a special **vital force** or vital energy (*the doctrine of vitalism*), without which compounds of this type could not be produced artificially in the laboratory. Since from the beginning of the nineteenth century an ever increasing number of substan-

ces common to the world of animals and plants were detected (beginning with acids, such as oxalic and formic, up to fats and proteins), the borderline between the chemistry of plants and that of animals gradually disappeared. When it became clear that the chemistry of plants and the chemistry of living organisms must be integrated into a single science, the new branch of chemical science was named *organic chemistry*. The credit for this goes to the notorious Swedish chemist J. J. Berzelius (1779-1848). Following A. L. Lavoisier (1743-1794), he made extensive use of quantitative analysis in his studies, discovered a number of new elements, established the atomic weights of many elements, discovered the phenomenon of isomerism and worked out the dualistic electrochemical theory.

Organic chemistry was considered to include not only substances isolated directly from plant and animal sources (which could not be obtained by synthesis according to the views of that time) but also the products of their chemical transformations. In 1824, the German chemist Friedrich Wöhler (1800-1882) produced oxalic acid, an organic compound, through the hydrolysis of cyanogen, of recognized mineral origin. An important discovery was that of Wöhler who in 1828 found that urea, a typical organic substance that derives its name from urine, in which it is found, could be prepared from the "inorganic" compound ammonium cyanate:

$$NH_4CNO \longrightarrow NH_2—CO—NH_2$$

It is this discovery that made a break in the wall of prejudices that separated organic chemistry from the chemistry of compounds of inanimate origins, and led the chemists of the time to believe that organic substances could also be produced artificially, without the intervention of a hypothetical vital force. Wöhler's discovery, however, did not immediately demolish vitalism. How firmly these erroneous views still persisted follows from the words of the French chemist Charles Gerhardt who developed certain fundamental concepts of organic chemistry (for example, the concept of homology) and was one of the authors of the Avogadro-Gerhardt law. In 1842, when many simple organic substances had already been obtained in the laboratory, Gerhardt held the view that the synthesis of such a complex compound as sugar could never be accomplished. This sceptical prediction was discredited in 1861 when A. M. Butlerov first obtained synthetically sugar substances from formalin. This was paralleled by the rapid growth of the number of individual carbon-containing compounds that did not occur in nature. Thus, in 1825, Faraday prepared benzene; ethylene, ethylene bromide, and a number of derivatives of benzene had become known still earlier. In 1842, Zinin obtained aniline from nitrobenzene, and in the fifties of the same century the first aniline dyes—mauveine (Perkin's mauve) and fuchsin—were synthesized from aniline.

As far back as the 1830's it became quite clear that organic chemistry should be defined in different terms, not as the chemistry of compounds of animate origin. It was at that time that Leopold Gmelin (1788-1853) defined the science of organic chemistry as the chemistry of carbon compounds, which continues to be a rather accurate concept up to the present time.

With this definition of organic chemistry there arises, however, a question: Is there anything special about carbon that makes it so unique among the other elements? Well, there is. This follows from a comparison of certain facts from organic and inorganic chemistry. First, the total number of known carbon compounds exceeds, at least by a factor of 10, the total number of known compounds formed by other elements without carbon. But even 2,000,000 organic compounds that have been investigated up to now by no means exhaust the boundless possibilities of designing organic molecules.

A particularly important development in organic chemistry was the discovery of the phenomenon of **isomerism** by Berzelius, which applies to the entire science of chemistry but is especially widespread in organic chemistry. The phenomenon consists in the existence of several compounds (and of many compounds in organic chemistry) which have the same composition and molecular weight but differ in the manner in which the constituent elements are combined in the molecule. It is no simple matter to cite an example of isomerism from the inorganic world (e.g., acid ammonium sulphate, NH_4HSO_4, and hydroxylamine disulphite, NH_3OHSO_3H, are isomers). But in organic chemistry, even among substances of the simplest composition, formed exclusively by carbon and hydrogen, the phenomenon of isomerism has led to the existence of a very large variety of chemical entities. It will suffice to say that to the composition $C_{20}H_{42}$ there must correspond 366,319 different hydrocarbons isomeric to one another, and that 4,111,846,768 different compounds have the composition expressed by the general formula $C_{30}H_{62}$, which outnumbers by thousands of times the total number of known organic compounds.

A second factor responsible for an enormous number of organic compounds is the phenomenon of **homology** discovered by Gerhardt. It consists in the existence of chemically similar series of compounds in which the structural formula of each differs from the immediately preceding and following ones by a CH_2 unit. Any compound in such a **homologous series** is termed a **homologue** of the others. The relationship between members of a homologous series is termed homology.

A third factor is the existence of **isologous series** of compounds, i.e., series of compounds built up of the same number of carbon atoms but differing in composition in such a manner that the molecule of each member contains two hydrogen atoms less than the preceding

member in the series (for example, ethane, C_2H_6; ethylene, C_2H_4; acetylene, C_2H_2). Even in the case of hydrocarbons, the simplest organic compounds, because of these factors there are strictly systematized series which form in fact a limitless multitude of substances.

It should also be noted that all oxygen- and nitrogen-containing and other organic compounds may be regarded as compounds related to a definite hydrocarbon. It may be visualized that they originate from the corresponding hydrocarbon through the replacement of one or more hydrogen atoms by groups containing atoms of oxygen, nitrogen, etc. This circumstance allowed Schorlemmer to define organic chemistry as the chemistry of hydrocarbons and their derivatives.

While the phenomenon of isomerism is very seldom encountered in inorganic chemistry, homology and isology are not observed at all. What stands behind this difference from organic chemistry? In order to understand better the cause of this difference, it is useful to consider briefly how it was gradually elucidated during the development of the science.

In the nineties of the eighteenth century Lavoisier revealed the important role of oxygen discovered not long before that time. Examining substances containing oxygen (oxides), he defined the remaining portion of an oxide as a base or radical. Oxides were then classified as basic and acid, which interact with the formation of salts. Taking into account the then established relationship between chemical and electrochemical phenomena (the discovery of the voltaic pile which generates electricity due to a chemical reaction; the use of this chemical source of current by Davy for decomposition of salts; the discovery of the laws of electrolysis by Faraday), Berzelius enunciated the notorious **electrochemical theory** of chemical affinity (the dualistic theory). According to Berzelius, the atom of an element, being electropositive, combines with oxygen which is electronegative; the charges become neutralized upon the combination. This neutralization, however, is incomplete: since the charge on the metal is higher than that on oxygen, basic oxides bear a net positive charge, while acid oxides carry a net negative charge. It is for this reason that basic and acid oxides combine with each other to form salts. Thus, "sodium sulphate consists not of sulphur, oxygen and sodium, but of sulphuric acid and sodium hydroxide, each of which can in turn be decomposed into an electropositive and an electronegative part" (Berzelius). In its crude form the dualistic theory anticipated the **ionic theory** (1887) of another Swedish scientist, Svante Arrhenius (1859-1927).

Berzelius considered his theory to be applicable also to organic chemistry, the only difference being that in organic compounds the radicals in oxides are more complex, for example, hydrocarbon radicals (and not elements).

The general recognition of this viewpoint was wavered when the

French chemist Jean-Baptiste Dumas (1800-1884) discovered the law or **theory of substitution** (1834) to which he gave the name of **metalepsy** (from a Greek word meaning "exchange"). Dumas found that when certain organic compounds were acted on by chlorine, the latter exhibited the power of abstracting hydrogen (which was removed in the form of hydrogen chloride) and of replacing it, volume for volume, or atom for atom. In this process, the chemical character of the compound is not substantially altered; for example, the chlorination of acetic acid results in the successive formation of monochloroacetic, dichloroacetic and trichloroacetic acids, which are monobasic, like acetic acid. This led Laurent to the conclusion (1835) that, as a result of the substitution reaction, chlorine enters a compound and takes the place which was occupied by hydrogen. The arrangement of atoms in a molecule had thus come to be understood as the decisive factor: what is important here is the type of a compound rather than the chemical nature of the constituent atoms in the molecule.

This was the **theory of types** put forward by Laurent (1807-1853). The contradiction to the dualistic electrochemical theory of Berzelius, which was in good agreement with the facts of inorganic chemistry (the chemistry of acids, bases and salts, i.e., that of electrolytes), was striking: chlorine, a negatively charged element, takes the place and, as it were, plays the part of the hydrogen, a positively charged element, which is removed. The chlorinated product, therefore, is not essentially different in chemical character from the original substance. It was established later that chlorine was not an exception: hydrogen was found to be capable of being replaced (directly or indirectly) by the other halogens and electronegative elements such as oxygen, sulphur, etc., and the electrochemical dualism of Berzelius was strongly shattered. The unitary theory (theory of types) became dominant. Radicals had even earlier gradually come to be regarded as invariable constituent parts of organic compounds (like the elements in inorganic compounds), which pass in reactions from one compound into another. Many investigations, especially those carried out by the German school (Wöhler, Liebig), stimulated by the discovery of a series of new elements, were guided by the search for new radicals. Such radicals passing unchanged from compound to compound were found to be in most cases oxygen-containing formations, say, the benzoyl radical C_6H_5CO or C_7H_5O (which enters into the composition of benzoic acid, C_6H_5COOH; benzoyl chloride, C_6H_5COCl; benzaldehyde, C_6H_5CHO, etc.) and the acetyl radical CH_3CO or C_2H_3O. Berzelius disputed the inclusion of oxygen in a radical, regarding it to be nonsense from the standpoint of both the concept of a radical as a part of a compound linked to oxygen (Lavoisier) and the electrochemical dualism. He suggested, for example, recognizing the residue C_7H_5 as the radical

of benzoic acid, and C_2H_3, as the radical of acetic acid. The definition of a radical as a part of a compound that remains unchanged in reactions (given by the German school of chemists) was found, however, to be more accurate. According to this viewpoint, oxygen passes from compound to compound together with the remaining portion of the radical, forming one whole with it. The assumption of the existence of oxygen and also of chlorine and some other elements within a radical (in place of hydrogen) was destined to give birth to the unitary theory (theory of types).

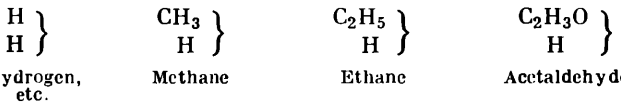
Numerous attempts to isolate radicals in a free state either proved unsuccessful or led to erroneous results. Thus, before the enunciation of the Avogadro-Gerhardt law, ethane isolated by the Wurtz reaction:

$$2CH_3Br + 2Na \longrightarrow CH_3-CH_3 + 2NaBr$$

was regarded at first to be a radical—a methyl group CH_3 and only the subsequent determination of its molecular weight showed its doubled value. Furthermore, it became more and more evident that no unalterable radicals existed and that radicals passed unchanged into newly formed molecules in some reactions or undergo changes in others. The concept of a radical gave way to the **theory of residues** (Gerhardt), in which a residue was regarded as a part of a molecule that was capable of surviving in a given reaction but might be different in other reactions.

Attempts to find something common in the nature of organic molecules forced scientists to abandon fruitless searches for the unalterable part of the molecule and to take up observing the most changeable part, the one we now call the functional group. These observations led to the introduction of the **new type theory** by Gerhardt, which was an extension of the older theory of types (Laurent). Alcohols and acids were looked upon by Gerhardt as the analogues of water, the chlorine derivatives of hydrocarbons as the analogues of hydrogen chloride, and the amines discovered at the time by Wurtz as the analogues of ammonia. In this way there were established the types H_2O, HCl, H_3N, and H_2. The replacement of hydrogen in these typical inorganic molecules by organic residues (formerly, radicals) with all their homologous and isologous possibilities was considered to be responsible for a large variety of organic compounds, which were arranged in the following series:

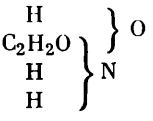
$\left.\begin{matrix}H\\H\end{matrix}\right\}O$	$\left.\begin{matrix}CH_3\\H\end{matrix}\right\}O$	$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O$	$\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O$
Water	Methyl alcohol	Ethyl alcohol	Acetic acid
$\left.\begin{matrix}H\\Cl\end{matrix}\right\}$	$\left.\begin{matrix}CH_3\\Cl\end{matrix}\right\}$	$\left.\begin{matrix}C_2H_5\\Cl\end{matrix}\right\}$	$\left.\begin{matrix}C_2H_3O\\Cl\end{matrix}\right\}$
Hydrogen chloride	Methyl chloride	Ethyl chloride	Acetyl chloride



Hydrogen, etc. Methane Ethane Acetaldehyde

The relationship between such series is termed **heterology** and the series themselves are called **heterologous series.**

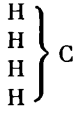
In 1851, Alexander Williamson (1824-1904) introduced the concept of **multiple types,** e.g., double and triple water types, in which radicals are capable of replacing two or more atoms of hydrogen. At a later time, some substances were assigned to two or more types (**mixed types**). For example, aminoacetic acid may be regarded as belonging to the ammonia and water types:



Aminoacetic acid

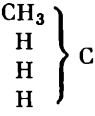
Such compounds are now termed as heterofunctional compounds.

An important step forward was made by the German chemist Friedrich August Kekulé (1829-1896), who added the **marsh gas type** to the known types:



Methane

Kekulé made a systematic use, in the organic chemistry of organogenetic elements, of the doctrine of **valency** introduced into chemistry by the English scientist E. Frankland (the word valency or valence was coined by A. W. Hofmann), who worked it out as a result of investigations into the composition and molecular weights of volatile organometallic compounds. In 1857, Kekulé extended the concept of valency to the element carbon. The recognition of the quadrivalency of carbon soon led Kekulé to the necessity of recognizing the ability of carbon to unite with itself, atom by atom, to form open and closed chains. For example, the formula for ethane was written in the following manner:

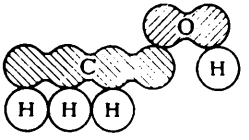


Ethane

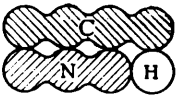
Carbon was found to be capable of forming also a long chain of atoms, which may contain tens and, as we know today, hundreds and thousands of carbon atoms.

For carbon and oxygen to retain their constant valency, it proved to be necessary to assume also the existence of a double bond in such compounds as ethylene (the C=C bond), aldehydes and ketones (the C=O bond).

Kekulé's formulas were as follows:

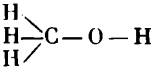


Methyl alcohol

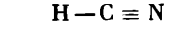


Hydrocyanic acid

The Scottish chemist Archibald Scott Couper (1831-1892) proposed representing the constitution of compounds by means of graphic formulas in which, as at the present day, the valencies of the atoms are represented by lines. Couper's formulas may be exemplified by the following:



Methyl alcohol



Hydrocyanic acid

The idea of the intimate relationship between the chemical (and physical) properties of the molecule and its structure, expressed by a formula, the idea of the uniqueness of this structure, was however unknown to Kekulé and Couper. This showed itself in the number of different formulas used to represent the composition of a compound, depending on the set of reactions to be described by the formula. These were basically the so-called **reaction formulas.** In 1861, A. M. Butlerov enunciated his structural theory (it was Butlerov who coined the term chemical structure or constitution).

According to Butlerov, **chemical structure** is the sequence in which the atoms are bound in the molecule. He showed how the structure of a given substance and its structural formula could be established on the basis of a study of chemical reactions (each compound being represented by a single unique structural formula). According to this formula, it is possible to synthesize the given compound. The properties of an atom in a compound depend primarily on the atom with which it is linked. Thus, the properties of a hydrogen atom linked to oxygen are different from those of a hydrogen attached to carbon, and if these properties are known, the atom with which the atom of interest is bound can be identified. As an example, the hydrogen atom linked to oxygen, as in alcohols, is capable of being replaced by sodium (just as the hydrogen in water—an inorganic prototype having the same bonding character), whereas the hydrogen attached to a carbon atom is usually inert with respect to sodium. The pro-

perties of a given atom are also affected by its other neighbours which are not directly linked to it. Though this influence is weaker, it has nevertheless to be considered in establishing the chemical structure.

The structural theory absorbed the theory of radicals since any part of the molecule that passes in a reaction from one molecule to another was what in earlier years had been called a radical (residue), but with no prerogative invariability. It also absorbed the theory of types as the inorganic or carbon-containing groups present in the molecule, whose origin could be traced out to water (the hydroxyl OH), ammonia (the amino group NH_2), carbonic acid (the carboxyl $-C\begin{matrix}O\\ \diagup\!\!\diagdown\\ OH\end{matrix}$), etc., determined, in the first place, the chemical behaviour (function) of the molecule and rendered this behaviour similar to that of the prototype. It is immaterial whether, for example, in methyl alcohol, CH_3OH, the methyl group takes the place of the hydrogen atom in water or the hydroxyl group replaces the hydrogen in methane, CH_4.

It should be noted that, in general, structure must be established every time a chemical reaction is carried out and a reaction product isolated, and a considerable part of a course of organic chemistry is devoted to this problem. For the structure of a compound to be determined it is necessary to make certain that an individual substance has been isolated, to know its quantitative elemental composition and molecular weight. If its composition and molecular weight are known, then, as will be shown at a later time, the *molecular formula* of the compound can be set up, i.e., a formula that gives the number of atoms of each element in the molecule. How the problem of structure is to be solved by chemical means may be illustrated by a few simple examples. Suppose we have two individual substances: a gas with a boiling point of —24°C and a liquid with a boiling point of 78°C, which have the same molecular formula C_2H_6O, i.e., are isomers. How could we establish the sequence of bonds between the atoms in their molecules, i.e., how could we derive their structural formulas? To do this, it is necessary to study the reactions of both substances.

The liquid substance reacts with sodium according to the water type, liberating one atom of hydrogen for one atom of sodium, the sodium atom taking the place of the hydrogen which is removed:

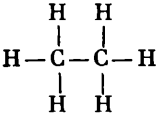
$$2C_2H_6O + 2Na \longrightarrow H_2 + 2C_2H_5ONa$$

That a second sodium atom cannot be introduced into the resultant solid derivative of sodium is proof that one of the hydrogen

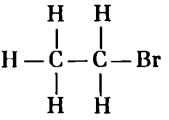
atoms was bonded differently as compared with the others, and that the group of atoms, of which it was a component part, also belonged to the water type. Thus, we easily arrive at a conclusion that the liquid substance contained a hydroxyl group. Isolating it, we can write the formula of the compound: C_2H_5OH. A confirmation of this conclusion is that when the original liquid substance is reacted with phosphorus tribromide, the hydroxyl group as a whole leaves the molecule and joins the phosphorus atom, being substituted by bromine:

$$3C_2H_5OH + PBr_3 \longrightarrow 3C_2H_5Br + P(OH)_3$$

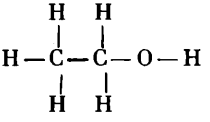
Further, if C_2H_5Br is allowed to react with zinc dust in an aqueous-alcoholic solution, the gas ethane, C_2H_6, will be evolved, in which two carbon atoms are joined together. Taking into account that carbon has a valency of 4 and hydrogen a valency of 1, the structure of ethane may only be represented as follows:



Then, the following structure should be assigned to the substance C_2H_5Br:



As regards the starting liquid substance (with a boiling point of 78°C), it is found to have the following structural formula:

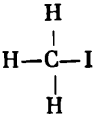


that is, the structure of ethyl alcohol (ethanol). The gaseous substance isomeric to it does not react with metallic sodium and on interaction with hydrogen iodide decomposes according to the equation (in terms of molecular formulas):

$$C_2H_6O + HI \longrightarrow CH_3I + CH_4O$$

On this basis we can draw a conclusion that the two carbon atoms in the gaseous substance are not linked to each other as hydrogen iodide is incapable of breaking the carbon-carbon bonds. Besides, it has no special hydrogen atom capable of being replaced by sodium. After the molecule of this substance has been broken down by the

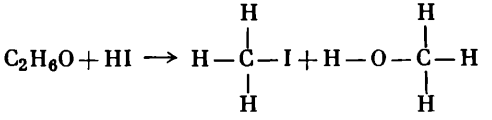
action of hydrogen iodide, CH_4O and CH_3I are formed. No structure other than



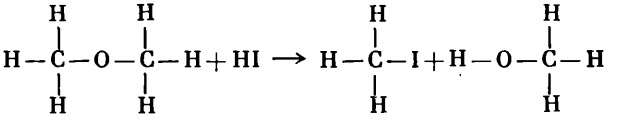
can be assigned to the latter substance because hydrogen and iodine are univalent. The second of the substances formed (CH_4O) behaves in reactions with sodium and phosphorus tribromide like ethyl alcohol:

$$2CH_4O + 2Na \longrightarrow 2CH_3ONa + H_2$$
$$3CH_4O + PBr_3 \longrightarrow 3CH_3Br + P(OH)_3$$

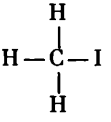
Thus, this is an alcohol containing a methyl group linked to a hydroxyl group. The reaction of the initial gaseous substance with HI may be written as follows:



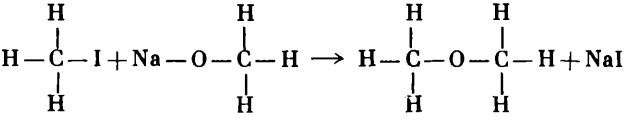
It would be natural to suppose that HI has broken the bond between the two methyl groups via an oxygen atom:



Indeed, when one of the products of this reaction, namely



is allowed to react with a sodium derivative of the other one:



we can synthesize the original gaseous substance which is isomeric with ethyl alcohol and thus confirm the suspected structure of dimethyl ether.

For more complex molecules the elucidation of structure is found to be much more complicated. First, one strives to determine, by

means of qualitative and quantitative reactions, the presence of functional groups in the molecule. The next step is to ascertain the sequence in which the carbon atoms are linked to one another, i.e., the carbon skeleton of the molecule. This task is fulfilled by gradual degradation of the molecule—breakdown (usually through oxidation) into smaller molecules—the fragments of the previous one, with subsequent elucidation of the structure of the products of degradation.* Knowing the structure of the fragments, one can try to visualize the structure of the entire molecule. Such a hypothetical formula must then be verified by means of other degradation processes which would give rise to other fragments. The final step in the derivation of the structural formula of the compound is the synthesis of this compound. Examples of structure elucidation for complex compounds can be found throughout the book.

The structural theory put forward in 1861 has served and continues to serve at present as the pivot in the development of organic chemistry. In addition to purely chemical means for the determination of the structure of organic compounds, numerous physical methods have been devised, which will be discussed later in the book. Though chemical methods continue to be of value, physical techniques such as mass-spectrometry, nuclear-magnetic resonance and optical spectroscopy become increasingly important.

Thus, a large variety of organic compounds, the possibility of formation of homologous series and the frequent manifestation of isomerism are all a direct consequence of the ability of carbon atoms to form chains (practically infinite) of interconnected atoms and to become firmly bonded both with electropositive (e.g., hydrogen) and electronegative (the halogens, oxygen, sulphur, nitrogen, etc.) elements, the atoms of some elements being capable of replacement by others without disturbing the general character of the molecular structure. Apart from carbon, only a few elements are known, which are able to form chains, very unstable at that, consisting only of a few identical atoms (such are nitrogen, sulphur, silicon). In most cases, the number of atoms is restricted to two (H_2, O_2, N_2, HO—OH, $H_2N—NH_2$, etc.).

On the basis of what has been said, with account being taken of the historical development of the chemical thought with all its achievements and failures, such as the collapse of the dualistic electrochemical theory of Berzelius, we can give the following simplified definitions of inorganic and organic chemistry.

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* In 1920 F. W. Aston introduced a new method of investigation—mass-spectrometry, with the aid of which isotopes of stable elements were discovered. Since the beginning of the second half of this century mass-spectrometry has been used in organic chemistry as a powerful method for the degradation of organic compounds and elucidation of their structure (see Volume II).

Inorganic chemistry is predominantly the chemistry of polar compounds and polar chemical bonds, whereas *organic chemistry* is largely concerned with study of non-polar compounds and non-polar chemical bonds. The specificity of the carbon atom consists in that it readily forms stable non-polar bonds both with electropositive and electronegative elements.

We have thus approached the problem of the nature of the chemical bond, the problem which had been abandoned since the time of Berzelius and which revived in the twenties of this century.

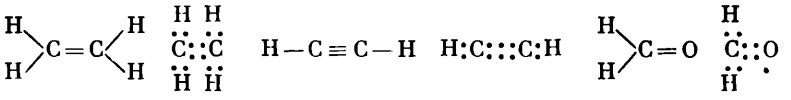
The theory of electrolytic dissociation laid the foundation of the ionic theory of the structure of salts and other electrolytes. The discovery of the electron, which was a logical culmination of the quantitative laws of electrolysis put forward by Faraday, was another prerequisite for the creation of the **theory of electrovalency.** It has been found that the most characteristic chemical act is the formation of cations and anions which are held together by simple electrostatic forces of attraction. Cations are formed by atoms of metals that lose their electrons which are captured by other atoms to yield anions. This concept was most fully and consistently used by W. Kossel (1917) with respect to compounds and processes in inorganic chemistry. It was, however, clear even to Kossel that non-polar (or homopolar) substances (e.g., diatomic molecules of such elements as hydrogen or nitrogen, hydrocarbons) should be considered from a different viewpoint. Such an approach was developed by G. N. Lewis in 1916, but his theory became generally known only after World War I. The main postulate of the Lewis theory, which remains valid for the overwhelming majority of organic compounds, is the formation of a chemical bond in non-ionic compounds* (the **covalent bond**). The covalent bond results when two electrons, one from each atom, are shared equally by each atom and do not belong exclusively to one alone. Thus, to ordinary formulas there correspond the following Lewis formulas:

H_2	CH_4	C_2H_6	CH_3CH_2OH
	H	H H	H H
H:H	H:C:H	H:C:C:H	H:C:C:O:H
	H	H H	H H

To each line (bond) in the theory of structure there correspond two dots symbolizing a pair of bonding electrons. In the case of a double bond two electron pairs are involved in bond formation, and the

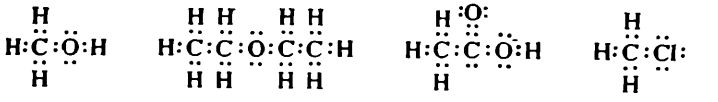
* It is found, experimentally, that chemical compounds can be placed in two broad classifications: those that conduct electricity in solution or in the molten state (ionic compounds) and those that do not (non-ionic compounds).—*Tr.*

sharing of three pairs of electrons corresponds to a triple bond.* For example, ethylene, acetylene and formaldehyde may be represented in the following way:

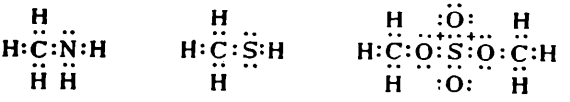


Ethylene Acetylene Formaldehyde

Carbon is invariably surrounded by eight electrons (a complete octet), the same stable group of electrons as in the outer shell of the nearest inert gas, neon, and hydrogen has only two electrons, which corresponds to the electron shell of the helium atom. According to the Lewis theory, all the other organogenetic elements are also surrounded by the electron shell of the nearest inert gas (Ne or Ar)—by an octet of electrons. But while in an inert gas the octet belongs completely to the atom of the element, in carbon the electrons of the octet are fully shared (in pairs) by carbon and by the atoms linked to it. In other elements (O, N, S, the halogens), some of the four electrons of the octet are shared, forming covalent bonds, and the others are in the form of free pairs, as seen from the following formulas:



Methyl alcohol Diethyl ether Acetic acid Methyl chloride

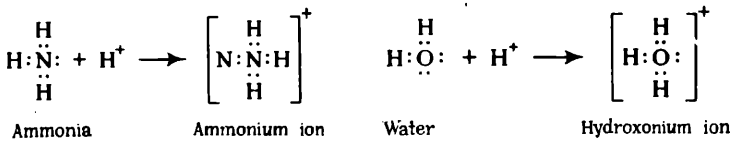


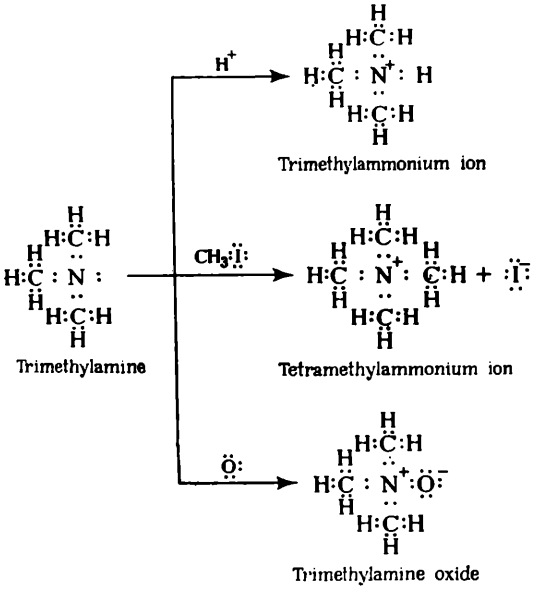
Methylamine Methyl mercaptan Dimethyl sulphate

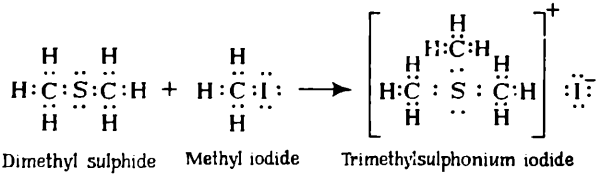
The limiting character of an octet (meaning that the atom surrounded by an octet of electrons cannot accept or share new electrons) and the presence of free pairs of electrons allowed Lewis to draw an important conclusion that the atoms of such elements exhibit a new kind of valency. An atom that has free pairs of electrons, say, the atoms of oxygen, sulphur, and particularly nitrogen, can share

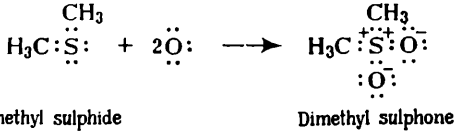
* It will be shown later that the first bond in the double (and triple) bond is more stable (the so-called σ-bond) and equivalent to a single bond and the second one is known as the π-bond, formed with the liberation of less energy and more labile physically and chemically (see Chapter 3).

these electrons with another atom possessing an incomplete octet or with an ion, thus forming a chemical bond. For example,









One should distinguish between two modes of formation of a chemical bond due to the donation of both electrons by only one of the atoms involved in bond formation. First, an ion (H^+ or $\overset{+}{C}H_3$ from

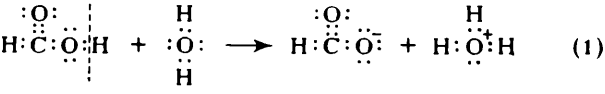
CH_3I in our examples) can share the free pair of electrons. Since the ion brings with itself its own charge, a cation of the so-called onium (ammonium, hydronium, sulphonium) compound is formed. The charge now resides not on the ion but on the central atom of the onium cation. As to the particle added (the former cation), it is linked now by an ordinary **covalent bond**—by a pair of electrons. In the ammonium ion, all the hydrogen atoms (or, accordingly, the methyl groups in the tetramethylammonium ion) are bonded with the central atom absolutely identically.

Second, a neutral atom which lacks one pair of electrons to attain the octet configuration, i.e., one which has a sextet of electrons, may share the free pair of electrons, just as the oxygen in the case of trimethylamine oxide. Then, the atom that donates its unshared electron pair acquires a positive charge. The acceptor atom (oxygen) acquires one full negative charge. As a result, these two atoms are found to be united to each other in a dual way—by a covalent bond, through an electron pair, and by an electrovalent bond, through full opposite charges. This type of chemical bond is known as the **semipolar** (or **donor-acceptor**) **bond.*** In the classical theory of structure, the donor-acceptor bond was represented just like the double bond, for example, $(CH_3)_3N{=}O$. Later, it was written more accurately as $(CH_3)_3\overset{+}{N}{-}\overset{-}{O}$ or a short arrow was used to designate such a bond: $(CH_3)_3N \rightarrow O$.

The presence of a donor-acceptor bond in a molecule has a strong effect on the physical properties: such substances have a higher boiling point, a higher dielectric constant, etc.

It may be said that Lewis overestimated the range of applicability of the octet rule and the occurrence of semipolar bonds. The octet rule holds only for the elements of the Periodic System from boron to fluorine (and neon) inclusive. Silicon, phosphorus, and sulphur may contain up to 12 electrons, which follows from the existence of such covalently bonded compounds as SF_6 or the anion SiF_6^{2-}.

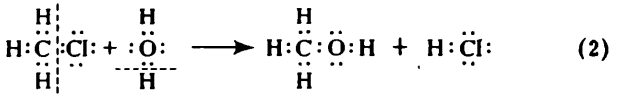
Even the conceptions formulated by Lewis may be used as a means of classifying reactions and reagents. Such a classification may be illustrated by some examples. Thus, in reactions (1), (2), (3), and (5) the chemical bonds are ruptured in an unsymmetrical manner, so that the electron pair, which was shared by two atoms, remains attached to one of the atoms:



(1)

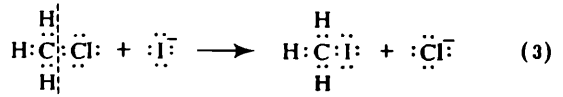
Dissociation of formic acid into ions

* The term *coordinate link* (Sidgwick) is now generally applied to such bonds. — *Tr.*



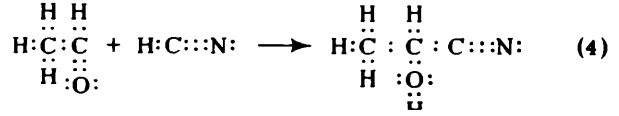
(2)

Hydrolysis of methyl chloride



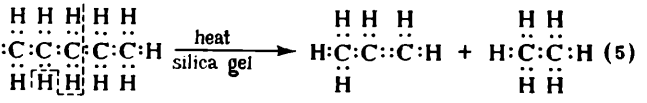
(3)

Exchange of Cl for I in methyl halide



(4)

Addition of hydrocyanic acid to acetaldehyde



(5)

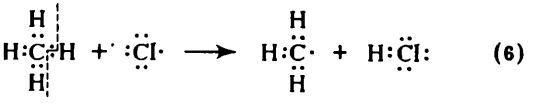
Catalytic cracking

Such an unsymmetrical splitting of an electron pair is termed **heterolytic cleavage** (or scission) or **heterolysis.** Ionization is a special case of heterolysis. That part of the molecule of each reagent to which a pair of bonding electrons is transferred and which carries, as a result, a negative charge, unites eventually with the oppositely (positively) charged portion of the molecule of its partner. The part of the molecule that gains the electron pair, which formed a bond earlier, is called **nucleophilic** (from the Greek words meaning nucleus loving; the nucleus of the atom is charged positively) since it is capable of attacking the positive charge and combining with a positively charged particle. In particular, any anion is nucleophilic in a varying degree. The opposite part of the molecule that has an atom with a sextet of electrons and carries a positive charge is **electrophilic** (electron loving). All cations are more or less electrophilic.

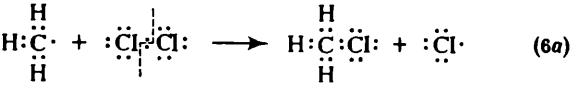
The terms nucleophilic and electrophilic are also used to define neutral reacting molecules, though a neutral molecule forms on heterolysis both a nucleophilic and an electrophilic part and, hence, it cannot, as a whole, be objectively assigned to either of these categories. In such cases the sense of the reaction is taken into account. For example, in reaction (3), evidently, not the sodium ion from sodium iodide attacks the chloride ion but, conversely, the iodide ion attacks the carbon of methyl chloride and, making a covalent bond with it, forms methyl iodide. In this sense, sodium iodide as

a whole is spoken of as a nucleophilic reagent (or a nucleophile), and methyl chloride involved in this reaction is termed as a whole an electrophilic reagent (or an electrophile). Analogously, for reaction (4), in which hydrocyanic acid (cyanide ion) attacks the positive carbonyl carbon of the aldehyde, the molecule of hydrocyanic acid is called nucleophilic (though, in principle, this name belongs to CN^-), and the molecule of the aldehyde is called electrophilic (though, in fact, this name refers to the carbonyl carbon). Thus, when two uncharged molecules react with each other by a heterolytic mechanism, two electrophilic and two nucleophilic parts of both reactant molecules are in fact operating in the reaction, but the nature and significance of the process are determined by one of the electrophiles and one of the nucleophiles and the two molecules are named accordingly.

An absolutely different type of reaction, with a **homolytic cleavage** of a bond (the breaking of a chemical bond in a symmetrical manner), may be represented by the following examples:

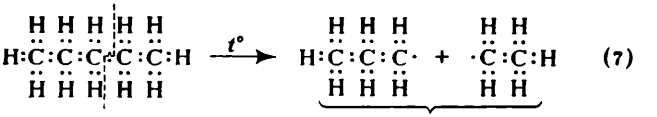


(6)



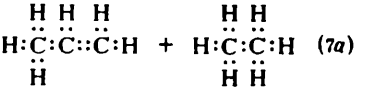
(6a)

Chlorination of methane by light

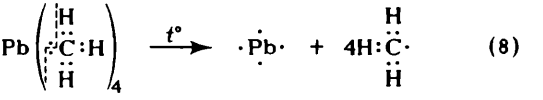


(7)

Thermal cracking

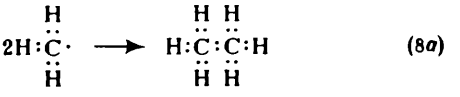


(7a)



(8)

Pyrolysis of tetramethyllead



(8a)

In homolysis, the two electrons constituting the bond are separated and two free radicals are produced, each having an odd, **unpaired electron.** Such free radicals* are usually very unstable and are instantly converted into stable molecules at the next stage of the reaction (often a chain reaction; see page 99), as shown in reactions (6a), (7a) and (8a).

Homolytic reactions proceed predominantly in the gas phase or in solvents of low dielectric constant, while heterolytic reactions take place largely in solutions, particularly in solvents having a high dielectric constant (water, anhydrous formic acid, dimethyl sulphoxide, dimethylformamide, etc.).

The above preliminary data on the classification of reactions and reagents have been tied up here with the Lewis theory, from which it undoubtedly emerged. It should be pointed out that these definitions and terms were in fact introduced at a later time by the English school of chemists (Lowry, R. Robinson, Ingold).

The conceptions formulated by Lewis serve, in most cases, as a fruitful addition and extension of the classical theory of structure. It must however be admitted that the concept of an electron as a charged point is primitive. An electron is not only a particle but also a wave and the nature of the chemical bond is largely determined by its wave properties. This aspect will be discussed later (see Sec. IV).

1.2. The Concept of a Chemical Entity

When the concept of the molecule was firmly established in science, the chemical entity (a simple substance or a compound) was meant to denote a substance consisting of identical molecules (a molecularly homogeneous compound).

In practice, it is of course impossible to attain a complete purity of a substance, and the purity requirements are different in different cases. For routine organic-chemical work, a sample with a content, say, of more than 99 per cent of the principal compound is said to be chemically pure. Compounds of a lower purity are often used, but sometimes an even higher purity is required.

An ordinary elemental analysis aimed at establishing the empirical formula of a compound provides little information about the purity of the substance. A substance is relatively heavily contaminated by other substances if the departure in elemental

* A free radical is an actually existing, though very short lived, uncharged (and, hence, containing an unpaired electron) fragment of a molecule. Free radicals must not be confused with radicals (residues)—mentally isolated parts of a molecule.

analysis exceeds a permissible error of 0.2 per cent. A compound is judged to be pure if its physical properties remain constant as purification proceeds. The physical properties used for this purpose are melting point (or freezing point), boiling point at a definite pressure, refractive index, density, spectral data, and, in certain cases, also specific rotation of the plane of polarized light. When a substance is to be purified for identification purposes, it is usually sufficient that its physical constants coincide with the reliable data available in the literature.

One must realize that the validity of such a criterion depends on the difference in the numerical data for the physical properties of an unknown substance and an impurity present. Naturally, if the physical constants for both substances are identical, then on further purification the constant will not change and the criterion cannot be applied. If we assume, for example, that the difference in the refractive indices of the compound and impurity is equal to 0.1, then, as the coincidence of the value of this constant for the same substance to within 0.001 is considered satisfactory, the detection limit of the method will be 1 per cent of impurity. Of course, methods of purification (separation of substances) and the accuracy of determination of physical properties can be improved without limit for special purposes.

It should be pointed out that none of the methods of characterization widely employed in organic chemistry and described in this book allow the separation of molecules of identical constitution, which contain different isotopes, such as ^{12}C and ^{13}C or ^{16}O, ^{17}O and ^{18}O. Even the separation of compounds containing hydrogen and deuterium (such compounds differ more significantly in physical and chemical properties) is incomparably more difficult than the separation of various substances with similar properties. Therefore, the data accumulated in organic chemistry refer to "natural" mixtures of compounds of the same constitution, whose molecules are built up of various isotopes.* Such mixtures have to be regarded as individual substances for ordinary purposes of organic chemistry. This introduces no inconveniences as the difference in the physical

* The most significant difference in the physical and reaction-rate constants is observed for compounds of deuterium and hydrogen. For example, deuterobenzene, C_6D_6, has a melting point of 6.5°C, a boiling point of 79.3°C and a relative density of $d_4^{20} = 0.9497$, while the corresponding values for benzene are: 5.5°C, 80.1°C, 0.9417. For deuterochloroform, $CDCl_3$, m.p. —64.15°C, b.p. 61.15°C, $d_4^{20} = 1.5004$; for chloroform: —63.90°C, 61.2°C, $d_4^{20} = 1.4880$. Since, however, the content of deuterium in nature is only about 0.016% with respect to hydrogen, the content of impurity molecules with this isotope is much lower than that of ordinary contaminants and cannot affect the constants of interest to the organic chemist. The content of ^{13}C mixed with ^{12}C is 1.1%; the content of ^{18}O found mixed with ^{16}O in water is 0.2%; the amount of ^{15}N mixed with ^{14}N is about 0.4%.

and chemical properties of the various molecules of this kind is negligibly small and is considerably lower than the accuracy limits of ordinary measurements. We have mentioned this for the simple reason that such impurities are not accidental and are always present and must be considered by the experimentor in very precise measurements.

The definition of an "individual substance" must, in principle, be revised and it should pertain only to compounds which are molecularly homogeneous and contain identical isotopes.

1.3. Separation and Purification Methods in Organic Chemistry

Whether a chemist is dealing with living or inanimate matter or with an artificially produced compound, he is invariably confronted with the task of separating an individual substance from a mixture of substances, which may sometimes be very complex. The physical separation methods used for this purpose are various types of distillation—fractional distillation at atmospheric pressure, high-vacuum distillation, molecular distillation; filtration and suction; crystallization; extraction; chromatographic techniques, in particular partition chromatography. Moreover, there are many other, highly specific methods, which are not applicable in every case. If the substance to be separated has a characteristic chemical function, say, is an acid or a base, the use of chemical methods will considerably facilitate its separation. The conversion of an acid or a base into a salt changes sharply the volatility and solubility of the substance. If the salt is insoluble, the substance is separated out as a precipitate, the precipitate is washed off from the impurities, and then the unknown substance is isolated in a free state by the action of a stronger acid or base. And if the salt is non-volatile, all the volatile impurities can be distilled off and the acid separated from the residue. In cases where the acid or base forms no water-insoluble salts, use may sometimes be made of the insolubility of these salts in organic solvents. It is because of the ease of identification of acids and bases that even in the eighteenth century and at the very beginning of the nineteenth century there were isolated and identified a number of organic acids and alkaloids (the latter possess basic properties).

Chemical methods of characterization of compounds, of course, require the simultaneous application of several physical procedures: precipitation, crystallization, distillation, etc., but in such a case the purification is much easier and requires no fractional separation techniques.

A. Distillation

Distillation at atmospheric pressure is carried out as follows: the liquid mixture is placed in a flask with a side arm (a Wurtz flask) or with a fractionating column, these being connected to a Liebig condenser (see Fig. 1.1) and is heated until the boiling point of the lowest-boiling component is reached. Into the flask are placed sealed capillaries or pieces of a porous plate (or some other source of air), without which boiling would proceed in a jumpwise manner

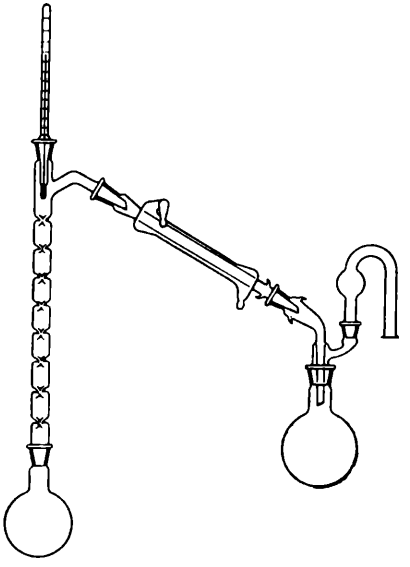


Fig. 1.1.
Distillation apparatus with a tree-like fractionating column.

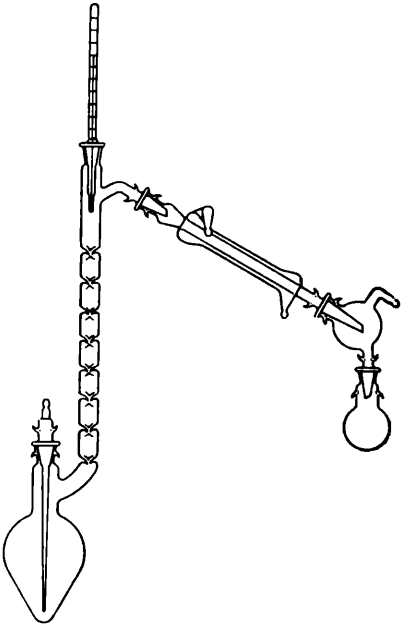


Fig. 1.2.
Apparatus for vacuum distillation.

because of the liquid being overheated. In the presence of air the liquid boils at a temperature at which its vapour pressure equals atmospheric pressure. It is clear that, apart from the boiling temperature, the atmospheric pressure determined by means of a barometer must also be recorded. After the distillation is complete all the non-volatile impurities remain behind in the flask and the vapours are carried over into the inner tube (adapter) of the condenser in which they are cooled and return to a liquid state, running into a receiving container. This method is applicable only if one substance (the one to be characterized) is volatile, i.e., when the vapour

pressure of the impurity is low at the boiling temperature of the substance to be identified. The thermometer with its bulb being streamlined by the vapours of the boiling substance immediately before the vapours are carried over into the condenser indicates the boiling range of the substance. A pure compound boils at a single fixed temperature—the boiling point.

Vacuum Distillation. If at atmospheric pressure a substance boils at such a high temperature that it undergoes partial decomposition, it is distilled off at a reduced pressure, the air being driven off from the system by means of a water pump (the residual pressure is 10-20 mm Hg) or by an oil pump (the residual pressure may amount to tenths or hundredths of a fraction of a millimetre of a mercury column). The substance is placed into a Claisen flask (Fig. 1.2). Into one neck of the flask is inserted, with a ground joint, a capillary so that it nearly reaches the bottom; the external end of the capillary is fitted with a length of a thick-walled tube gripped by a screw clamp. For a uniform boiling of the liquid to be attained during the distillation a current of air is carefully supplied under low pressure through the capillary. To the second neck of the flask is attached a thermometer in such a way that its bulb is just below the point where the vapour enters the side arm and is led to the condenser on heating the liquid. To the descending end of the condenser is connected, on a ground joint, an adapter with a receiving container. The air is sucked off from the system through the side arm of the adapter. The whole apparatus is sealed with the aid of ground joints.

If fractional distillation (see below) is required, special adapters and receivers are used (Figs. 1.3 and 1.4), which allow the receivers to be changed, without turning off the vacuum, and individual fractions or cuts boiling at constant definite temperatures to be separated.

Distillation in vacuum is applied to substances that boil above 200°C at atmospheric pressure. At a residual pressure of 20 mm Hg the boiling temperature decreases by about 100°C.

High-vacuum distillation is used to separate even higher-boiling compounds (300°C upwards) or compounds which decompose completely on heating without vacuum. At a residual pressure of 0.02-0.05 mm Hg the boiling temperature of such compounds is reduced by about 200°C.

Molecular Distillation. This type of distillation is employed to separate substances that decompose at the boiling temperature even in high vacuum. The principle of molecular distillation consists in the following: under high vacuum (10^{-5} to 10^{-8} mm Hg) at temperatures ranging from 50 to 300°C the molecules break loose away from the heated surface of the molten substance subject to distillation and pass, without boiling, to the gas phase; the mean free path of the molecules is so great that if the cold surface is placed

at a distance smaller than the mean free path of the molecules, the gas phase will be condensed on this surface. In this way, substances with a relatively high molecular weight and a weak structure can be purified. The principle of molecular distillation becomes clear by reference to Fig. 1.5 which shows a molecular still. In this case, the cold surface is simply a glass wall.

Steam Distillation. A substance boils at a temperature at which its vapour pressure equals atmospheric pressure. If a mixture of two

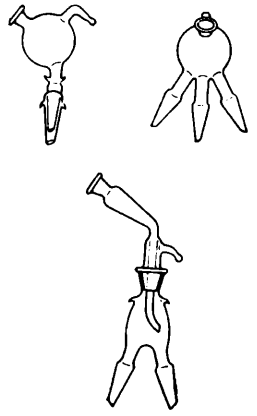


Fig. 1.3.
Types of adapters for fractional distillation in vacuum.

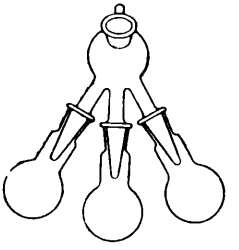


Fig. 1.4.
An adapter with receivers for fractional distillation in vacuum.

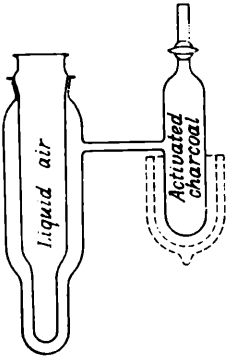


Fig. 1.5.
Apparatus for molecular distillation.

immiscible liquids is heated, they will boil at a temperature at which the sum of the vapour pressures of the two liquids will become equal to atmospheric pressure. The second liquid commonly used is water. Thus, the distillation of such a mixture of two liquids in a current of steam can be accomplished at a temperature lower than 100°C. Of course, water must not react or mix with the liquid to be identified. The operation is carried out in such a way that the vapour produced by boiling the water in a metal vessel (boiler) fitted with a protective tube, is delivered to the bottom of a special long-neck flask. The flask is placed in an inclined position to prevent the vigorously boiling liquid to pass into the condenser, to which the flask is connected through a side arm. The receiver collects two layers of liquid, water and the liquid to be distilled off, which are separated in a separatory funnel. The ratio of their amounts is determined by the ratio of the products of the vapour pressures of the substances involved (at the boiling temperature of the mixture) by their molecular weights.

For high-boiling substances to be distilled off, use may be made of ethylene glycol or glycerine (instead of water) which are similar to water as solvents and which do not mix with the majority of organic compounds. When glycerine is used, it is better to carry out distillation at a reduced pressure.

B. Fractional Separation of Substances Based on Phase Equilibrium

Many methods of separating a mixture into individual substances are based on the equilibrium distribution of two components between two phases—the liquid and the vapour phase (fractional distillation, gas-liquid chromatography); the solid and the liquid phase (fractional crystallization, adsorption chromatography); two liquids (extraction from a liquid, partition chromatography).

The separation of two substances consists in carrying out (batchwise or continuously) a successive series of operations, each of which is aimed at establishing an equilibrium between the two phases which contain the two substances in different proportions; thus, at equilibrium the phases A and B will contain the molar fractions of the first component, c_1, and the second component, c_2, and the separation factor will be expressed in the following way:

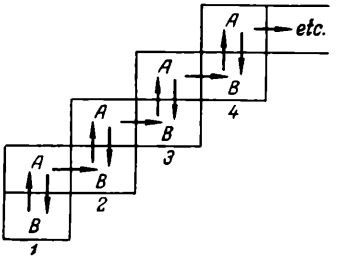


Fig. 1.6.
The stepping-off process for fractional separation of substances.

$$\alpha = \frac{\left(\frac{c_1}{c_2}\right)_A}{\left(\frac{c_1}{c_2}\right)_B} \tag{1}$$

It thus follows that the composition of phase A may be expressed in terms of the composition of phase B, in which case the separation factor will be:

$$\left(\frac{c_1}{c_2}\right)_{A,\,1} = \alpha \left(\frac{c_1}{c_2}\right)_{B,\,1} \tag{2}$$

(The subscript 1 signifies that these quantities refer to a single, once-through, operation.) The sequence of such equilibria (with subscripts 1, 2, 3, ...) may be represented by the diagram shown in Fig. 1.6.

In the rectification process outlined in the following section, the liquid phase B_1 is in equilibrium with the vapour A_1 being condensed to the liquid phase B_2, whose composition is evidently the same as that of the vapour A_1. The liquid phase B_2 is in equilibrium with its vapour A_2 which is condensed to the liquid B_3 having the same composition as the vapour A_2, etc.

In the case of solvent extraction the processes are the same: the liquid phase B_1 (which has dissolved the mixture of substances to be separated) is at equilibrium with the liquid phase A_1 which extracts the mixture at a distribution coefficient α. When the solvent is removed, the substance absorbed by the extractant phase is again dissolved in phase B (step 2 in the diagram) and extracted by the liquid A_2, and so on.

Fractional crystallization of a mixture of two or more substances proceeds in a similar way.

Since in all cases

$$\left(\frac{c_1}{c_2}\right)_{A(n)} = \left(\frac{c_1}{c_2}\right)_{B(n+1)}$$

we may write an equation for the second scheme of the separation process, relation (2) being taken into account:

$$\left(\frac{c_1}{c_2}\right)_{A(n)} = \alpha^{n-1}\left(\frac{c_1}{c_2}\right)_{A,1}$$

Fractional Distillation (Rectification). If two miscible liquids have an appreciable vapour pressure, the character of the curves showing the dependence of the boiling temperature of the mixture on the composition of the liquid, and the composition of the vapour over the liquid of a given composition at the boiling temperature may be expressed in three different ways (D. P. Konovalov), as shown in Fig. 1.7*a*, *b*, and *c*.

If the liquids do not react with each other but mix unlimitedly (for example, two hydrocarbons), the curve shown in Fig. 7*a* is obtained. The ordinates at points *A* and *B* (pure liquids) represent the boiling points of the liquids. The lower (evaporation or vaporization) curve shows the boiling point of the liquid as a function of the composition plotted along the horizontal straight line. The upper (condensation) curve expresses the composition of the vapour which is at equilibrium with the boiling liquid at each given temperature. Thus, a mixture of the composition determined by the point X_1 will boil at temperature t_1 and will yield a vapour of composition X_1' corresponding to the projection of point p_1 onto the horizontal axis (from point c_1). If this vapour (in the condenser) is condensed to a liquid (of the same composition) and is again heated to boiling, it will boil at a temperature given by the ordinate point c_2 (t_2) and will yield a vapour of composition X_2' corresponding to

the projection of point p_2, which can again be condensed to a liquid boiling at a temperature equal to the ordinate point c_3 and yielding a vapour of composition determined by the projection of point p_3 to the horizontal axis. The process is repeated (the stepping-off process from right to left, to the lower-boiling liquid) until the desired final composition (pure liquid A) is reached. If the composition

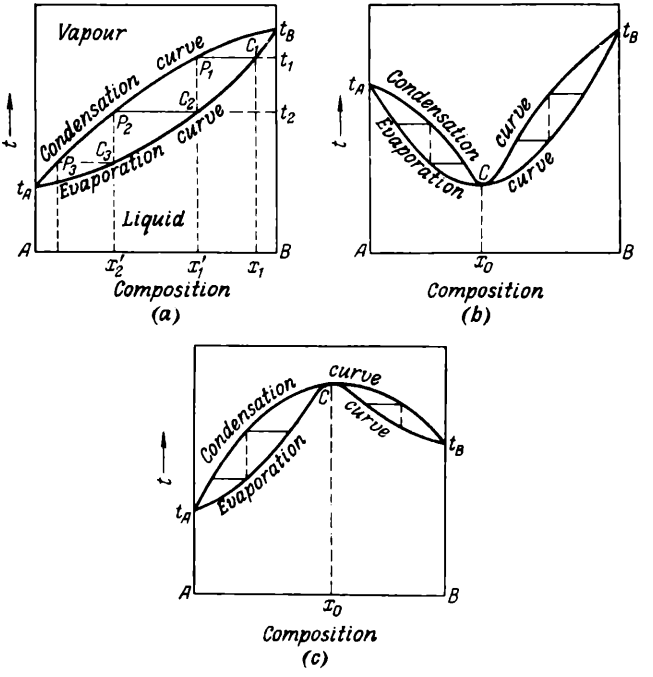


Fig. 1.7.

Temperature-composition diagrams:

(a) for mixtures of infinitely miscible liquids, for which the boiling point increases regularly; (b) for a mixture of two liquids forming a minimum boiling azeotrope; (c) for a mixture of two liquids forming a maximum boiling azeotrope.

of the liquid left in the distillation flask after each operation is traced in the same way, it will be enriched with liquid B, and the residue will be the pure high-boiling liquid B. What has been said refers, strictly speaking, to equilibria the establishment of which requires time and which are not actually attained during the distillation. For the equilibria to be approached as closely as possible, use is made of various types of apparatus for fractional distillation or rectification—fractionating or rectifying columns (Fig. 1.8; see also Fig. 1.1). In the column placed vertically on a distillation flask there takes place a partial condensation of the vapour; the resulting

liquid is returned to the top of the fractionating column (this condensate being called reflux) and allowed to flow down counter-current to the vapour rising up the column to the condenser.

In fractionating columns or in other, more perfect rectifying apparatus, the vapour is condensed in a reflux condenser above the column, the desired portion of the condensate being led into the receiver with the aid of a stopcock (see Fig. 1.8). The descending liquid (reflux) resulting from the condensation of the vapour and therefore enriched in the less volatile (heavy) component is brought into contact, in the lower narrow sections of fractionating columns or on the plates of large columns or else in the still heads of small columns, with a new portion of vapour rising counter-current to the reflux. This enables the equilibrium to be approached and hence provides a stepping-off process which has been described above.

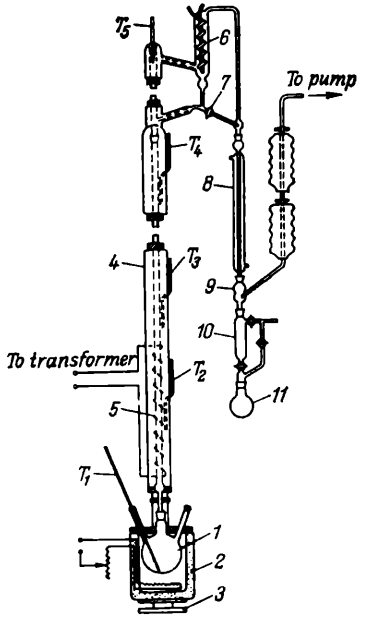


Fig. 1.8.

Distillation apparatus (80 theoretical plates):

1—distillation flask; *2*—electric heater; *3*—support; *4*—column; *5*—winding (resistance coil of one of heating segments); *6*—head; *7*—stopcock; *8*—condenser; *9*—funnel; *10*—Perkin receiver; *11*—round-bottomed flask; T_1-T_5—thermometers or thermocouples.

It is essential that adiabatic conditions be attained for the operation of the fractionating column, i.e., that proper insulation be provided in order to exclude at all or, at least, to minimize the heat exchange between the vapour (and the reflux) and the surroundings.

The effectiveness of various fractionating columns and modern laboratory rectifying columns is often expressed by the number of theoretical plates or theoretical stages of separation. Using the liquid-vapour composition diagram (for the entire boiling range), we can calculate the number of theoretical plates required to produce a change from the composition of the mixture to be fractionated to the desired composition at the specified rate of fractionation. This rate is measured by the so-called reflux ratio v:

$$v = \frac{R}{E} \tag{1}$$

where R = amount of liquid (reflux) returned to the column
E = amount of liquid taken off as overhead product for the same period of time.

The greater the reflux ratio, the more efficient is the separation and the slower the distillation. There is a "minimum reflux ratio" for each particular system, below which the desired separation could never be achieved.

The amount of vapour leaving the column (all the vapours are condensed to liquid D) is composed of the quantity of liquid R returned to the column as reflux and the quantity E withdrawn as distillate (the desired amount) into the receiver:

$$D = R + E \tag{2}$$

Let us denote the molar fraction of the more volatile (light) component in the vapour by Y and the molar fractions of the same component in the still liquid and distillate by X and X_E, respectively. Then, Eq. (3), which is similar to Eq. (2), will hold for the light component:

$$DY = RX + EX_E \tag{3}$$

Substituting the value of D into Eq. (3) yields

$$Y = \frac{RX}{R+E} + \frac{EX_E}{R+E} \tag{4}$$

Dividing the numerator and denominator of the right-hand side by E and taking relation (1) into account, we obtain the operating-line equation:

$$Y = \frac{vX}{v+1} + \frac{X_E}{v+1} \tag{5}$$

in which the molar fractions X and Y are variables at the specified value of X_E.

The operating line of a column expresses the dependence of the vapour composition, Y, on the composition of the liquid being rectified, X, for the given reflux ratio v and the desired composition of distillate, X_E. Let us plot the liquid composition X along the abscissa and the vapour composition Y along the ordinate in terms of the molar fractions of one of the components (for example, the more volatile component) of the mixture at normal pressure and varying temperature, which corresponds each time to the boiling point of the mixture of composition X.

Let us now determine, with the aid of Eq. (5), the reflux ratio as a function of the vapour composition Y at a fixed selected value of X equal to X_1:

$$Y = \frac{v}{v+1} X_1 + \frac{1}{v+1} X_E \tag{6}$$

Hence

$$v = \frac{X_E - Y}{Y - X_1} \tag{7}$$

The operating-line equation (5) corresponds to a family of straight lines (with different values of v) for the chosen vapour composition Y_E. At an infinite reflux ratio ($v = \infty$) the operating-line equation will be $X = Y$. Simultaneous solution of this equation and Eq. (5) gives the point of intersection D of any operating line (with different values of v) by an operating line with $v = 0$. These are the points with the coordinates X_E and Y_E (X_E being equal to Y_E) since the point lies on the operating line with $v = \infty$. The entire family of operating lines for the given X_E is enclosed between the two extreme lines, one of which is a bisecting line with $v = \infty$ and $X = Y$ and the other corresponds to the minimum reflux ratio v_{min}:

$$v_{min} = \frac{X_E - Y_1}{Y_1 - X_1}$$

The minimum reflux ratio is a function not only of the desired distillate composition (represented by X_E) but also of the original composition of the liquid being distilled off (expressed by X_1). For the original liquid composition X_1 and the vapour composition Y_1 which is in equilibrium with X_1 (in molar fractions of the more volatile substance) the operating line (a straight line) with a minimum reflux ratio passes through the point X_1Y_1 of the curve and through the common point of intersection of a family of operating lines for the distillate composition X_E.

Upon approaching an infinite reflux ratio the separation of the components is the most efficient but the process becomes infinitely slow and the amount of distillate tends to zero. The minimum reflux ratio is another borderline below which the desired separation could never be achieved.*

All the operating lines corresponding to the actually feasible lines (required to achieve the desired degree of separation) lie between the two limits. The diagram shown in Fig. 1.9 gives three operating lines: v_{min}, v_∞ and the intermediate one v_{real}. It is the stepping-off from the operating line to the liquid-vapour composition curve that represents the number of theoretical plates required to transpose the original liquid composition X_1 to the distillate composition X_E for the reflux ratio v chosen. The nearer the operating line is to the operating line with v_∞, the smaller the number of theoretical plates required for the separation, as seen from Fig. 1.9 (dashed-line and solid steps), but the slower is the process.

* The point is that graphically the stepping-off process cannot be started from the liquid-vapour composition curve by plotting a horizontal line from the point XY to the right until the line is intersected since the curve and the operating line (with a minimum reflux ratio) intersect precisely at this point.

The number of theoretical plates for a particular type of column can easily be found experimentally and so one can choose the column and the conditions of its operation (reflux ratio).

Let us consider equilibrium boiling temperature-composition curves (see Fig. 1.7*b* and *c*) corresponding to a case of weak interaction between the component liquids (solvation or association). One of these diagrams has a minimum boiling temperature and the other, a maximum boiling temperature, at which the liquid-vapour composition curves touch each other. The point representing the maximum or minimum boiling temperature divides the graph in two halves, each of which is similar to the curves shown in Fig. 1.7*a*, and the same reasoning applies to them. From the graph with the minimum boiling point it follows that, regardless of the original liquid composition, the fractionation process will yield a liquid of the composition corresponding to the minimum boiling point and the residue will be a pure liquid *A* or *B*, depending on whether we started with the composition corresponding to the left or right (from the minimum) portion of the curve. The situation is similar for the curve with the maximum boiling point, except that as the fractionation progresses the distillate is enriched in the pure liquid *A* or *B*, depending on whether the original composition corresponds to the left or right (from the maximum) portion of the curve; there will be left the liquid that approaches more and more to the composition corresponding to the maximum boiling point. The liquid compositions corresponding to the minimum and maximum of the curve are called constant-boiling or *azeotropic mixtures* (or *azeotropes*). They cannot be separated into their components by fractional distillation.

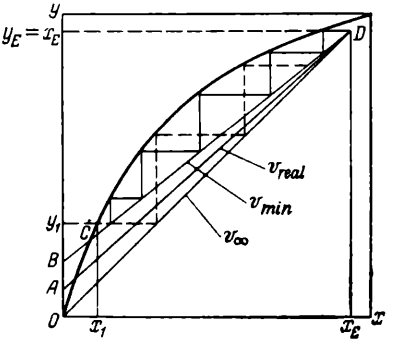


Fig. 1.9.

Operating lines for distillation: *OD*—at infinite reflux ratio (v_∞); *BD*—at a minimum reflux ratio for X_1 (v_{min}); *AD*—real operating line.

To separate an azeotrope into its components, any other physical method of separation must be used or else chemical methods must be resorted to. Still another alternative is to add a third liquid and produce a different azeotrope with a minimum boiling point, which would contain one of the two liquids that formed the first azeotrope; then, the other component that does not enter into the composition of the azeotrope could be separated by distillation. This procedure is frequently employed in practice. Some examples of a binary azeo-

trope with a minimum and a maximum boiling temperature are listed in Table 1.1.

An example of a constant-boiling mixture with a minimum boiling point is a mixture consisting of 95.5 per cent of ethyl alcohol and 4.5 per cent of water (the content of alcohol is 96 per cent by volume

TABLE 1.1. **Binary Azeotropes with Minimum and Maximum Boiling Temperatures**

Components		Azeotrope	
name	b.p., °C	composition, per cent by volume	b.p., °C
	With a minimum boiling temperature		
Hexane	69.0	73.1	50.0
Methanol	64.65	26.9	
Heptane	98.43	48.5	59.1
Methanol	64.65	51.5	
Cyclohexane	81.4	63.0	54.2
Methanol	64.65	37.0	
Cyclohexane	81.4	69.5	64.9
Ethanol	78.5	30.5	
Benzene	80.1	60.5	58.3
Methanol	64.65	39.5	
Benzene	80.1	67.6	67.8
Ethanol	78.5	32.4	
	With a maximum boiling temperature		
Acetone	56.5	20	64.7
Chloroform	61.2	80	
Methyl ethyl ketone	79.6	83.0	79.9
Chloroform	61.2	17.0	

or 96°), which boils at 78.15°C. Water boils at 100°C and anhydrous ethyl alcohol boils at 78.3°C. For 96° alcohol to be dehydrated, the water must be removed, say, by quicklime.

Crystallization. Solid substances are purified by recrystallization, for which purpose such a solvent or a mixture of solvents is chosen, in which the difference in the solubility of the substance on heating and in the cold would be large. The amount of impurities is of course much less than that of the principal substance and they remain in the mother liquor and do not crystallize. At a higher rate of crystallization (on rapid cooling of the heated solution) there are formed purer small crystals (there is a lesser amount of inclusions within

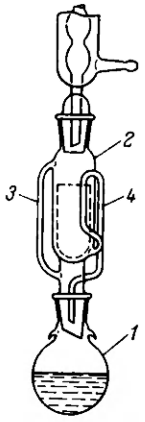


Fig. 1.10.

Soxhlet extractor for solids:

1—round-bottomed flask; *2*—extractor with a sleeve; *3*—vapour-delivery tube; *4*—tube for extract.

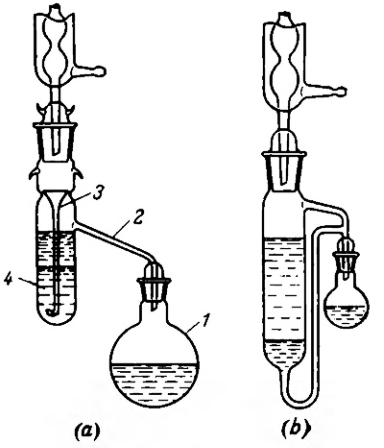


Fig. 1.11.

Extractors for extraction of liquids:

(*a*) by a liquid lighter than water; (*b*) by a liquid heavier than water; *1*—flask with an extracting liquid; *2*—side arm for removal of vapour and return of extractant; *3*—funnel tube; *4*—extractor.

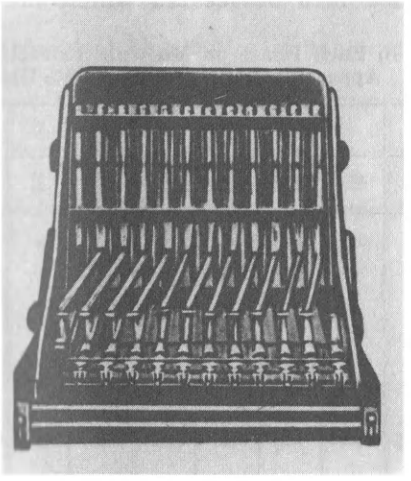


Fig. 1.12.

Apparatus for multiple fractional extraction (12 tubes). The position of tubes (cells) is changed by turning the metal spindle.

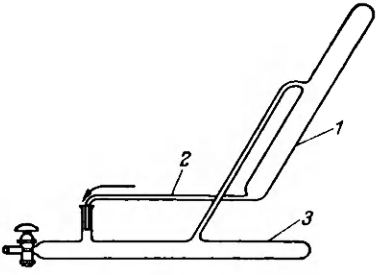


Fig. 1.13.

A single stage (cell) of the glass countercurrent apparatus for multiple fractional extraction:

1—extraction tube No. 1; *2*—overflow tube; *3*—extraction tube No. 2.

such a crystal). The mother liquor is separated by sucking in a Buchner funnel or any other similar device and by washing the crystals with a cold solvent. If a mixture of two or more substances present in comparable quantities is to be separated by crystallization into its components, fractional crystallization is employed.

Extraction. In many cases, at least for preliminary rough separation of a substance from a complex mixture, use is made of solvent extraction: the solvent chosen dissolves the desired substance and does not dissolve the other substances present in the mixture. The simplest apparatus for extraction (from solution) is a separatory funnel widely used in the laboratory. This is a round, pear-shaped or cylindrical, rather thick-walled vessel fitted with a stopcock at the bottom and a ground-glass stopper at the top. A solution of a mixture of substances (for example, in water) is shaken with a solvent that does not mix with the solution (the solvent chosen is usually ether or any low-boiling hydrocarbon or chloroform) as a result of which the desired substance passes (according to the distribution law) into the solvent. After separation of the phases the solvent is removed from the original solution by draining the liquid through the stopcock. The extraction with new portions of the solvent is repeated. There are special extractors for separation from the solid (Fig. 1.10) and the liquid phase (Fig. 1.11). The latter (liquid-phase) extractors are further classified into devices in which the

TABLE 1.2. **Amount of Solute in Each Phase on Multiple Extracti Apparatus with 12 Tubes; U = Up**

Tube	1		2		3		4		5	
	U	L	U	L	U	L	U	L	U	L
Initial state		1	—	—	—	—	—	—	—	—
Equilibrium after shaking	p	q	—	—	—	—	—	—	—	—
First transfer	—	q	p	—	—	—	—	—	—	—
Equilibrium after shaking	pq	q^2	p^2	pq	—	—	—	—	—	—
Second transfer	—	q^2	pq	pq	p^2	—	—	—	—	—
Equilibrium after shaking	pq^2	q^3	$2p^2q$	$2pq^2$	p^3	p^2q	—	—	—	—
Third transfer	—	q^3	pq^2	$2pq^2$	$2p^2q$	p^2q	p^3	—	—	—
11th transfer		q^{11}	pq^{10}	pq^{10}	p^2q^9	p^2q^9	p^3q^8	p^3q^8	p^4q^7	p^4q^7
Equilibrium after shaking	11	q^{12}	p^2q^{10}	pq^{11}	p^3q^9	p^2q^{10}	p^4q^8	p^3q^9	p^5q^7	p^4q^8

extractant is a liquid lighter than water (Fig. 1.11*a*) and those in which a liquid heavier than water is used as an extractant (Fig. 1.11*b*).

Especially important are devices for liquid-liquid extraction, which have played an enormous role in the isolation and characterization of organic substances from complex natural mixtures of plant or animal origin.

Figure 1.12 shows such an apparatus consisting of 12 extraction tubes, the operating principle of which becomes clear from Fig. 1.13. As an example, two substances present in an aqueous solution are to be separated. The apparatus is put in the position shown in Fig. 1.13. Water saturated with ether is poured into each extraction tube, except tube *1*, so that when the system is turned 90° the water fills the volume up to the side arm. Into tube *1* is poured, also up to the side arm, a solution of a mixture of two substances to be separated. Then an approximately equal volume of ether saturated with water is introduced into tube *1* (the extraction tubes being in the horizontal position). The apparatus is tilted 20-30 times and, after the liquid is allowed to stand for a while, is turned 90°, the ether extract overflowing into tube *2*, and then a new portion of ether is poured into tube *1* and the operation is repeated until the ether extract is in tube *12*. The most complete separation is achieved in tubes *1* and *12*, but usually even in tubes *2*, *3*, *4* and *9*, *10*, *11* the separation is sufficiently complete and only the two layers present

(Theoretical Distribution of Solute at Various Steps of Separation in an Phase and L = Lower Phase)

6		7		8		9		10		11		12	
U	L	U	L	U	L	U	L	U	L	U	L	U	L
—	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—	—	—
p^5q^6	p^5q^6	p^6q^5	p^6q^5	p^7q^4	p^7q^4	p^8q^3	p^8q^3	p^9q^2	p^9q^2	$p^{10}q$	$p^{10}q$	p^{11}	
p^6q^6	p^5q^7	p^7q^5	p^6q^6	p^8q^4	p^7q^5	p^9q^3	p^8q^4	$p^{10}q^2$	p^9q^3	$p^{11}q$	$p^{10}q^2$	p^{12}	$p^{11}q$

in the intermediate tubes contain a mixture of two substances. The two layers in the initial tubes contain the most water-soluble component, while those in the terminal tubes contain the most ether-soluble component.

The quantitative aspect of the extraction process is as follows. Let us make use of the unit of mass of each of the substances. Suppose the volumes of the solvents and the distribution coefficients for the two substances between them are such that after each shaking the upper organic (ether) phase contains a fraction p of one of the substances, and the lower aqueous phase a fraction $q = (1 - p)$. Data on the distribution of the desired substance between the tubes (for an apparatus consisting of 12 tubes) after each operation are presented in Table 1.2.

The fractions p and q depend on the distribution coefficient (distribution ratio) between the two phases. The greater the difference in the distribution coefficients of the two substances, the faster and more complete is the separation.

The distribution coefficient K of each of the substances between two phases is given by

$$K = \frac{\text{g/litre in the upper phase}}{\text{g/litre in the lower phase}}$$

or

$$K = \frac{p/v_{\text{ether}}}{(1-p)/v_{\text{water}}} = \frac{pv_{\text{water}}}{(1-p)\,v_{\text{ether}}}$$

Hence

$$p = \frac{Kv_{\text{ether}}}{Kv_{\text{ether}} + v_{\text{water}}}$$

where v_{ether} is the volume of ether, and v_{water} is the volume of water.

Substituting these values into the expression for the distribution in the nth operation (see Table 1.2), we shall find the concentration of each of the substances in the aqueous and ether phases in the extraction tubes as a function of the distribution ratio.

C. Chromatography

The technique of separation of a mixture of substances by adsorption (chromatography) discovered by the Russian scientist M. S. Tsvett at the beginning of this century has assumed great importance in the last several decades. No work in the laboratory is conceivable without this method. At present chromatography has differentiated into the following techniques:

(1) Column chromatography.
(2) Partition paper chromatography.
(3) Thin-layer chromatography (on a plate).
(4) Gas-liquid chromatography.

Column Chromatography (Adsorption Chromatography). The separation is effected by means of a glass tube filled with a powdered adsorbent. Use is most frequently made of alumina (a special grade for adsorption), silica gel, starch, and barium sulphate. In fact, any adsorbent that does not react with substances to be separated and with the solvents may be used for separation by this method.

A suspension of a solid adsorbent in the most indifferent solvent is prepared and poured into a tube fitted at the bottom with a filter or into a tube secured in the stopper of a small funnel with a filtering bottom. The time required for the column to be filled can be shortened by the application of suction at the bottom. Into the column packed in this way (Fig. 1.14), in which a free space is left at the top, is poured a solution of a mixture of compounds in the same indifferent solvent, which is allowed to filter through the column. The substances are partly adsorbed in the same zone and are partly separated. The least strongly adsorbed component comes down through the adsorbent to a somewhat lower level in the column. This is followed by what is known as **elution** (washing the bands out of the column), with the same or another solvent. The chromatographic column operates, in general, like a fractionating column, the substances subject to separation being distributed between the solid adsorbent phase and the liquid solvent phase. The two substances travel down the column at different rates. The adsorption zone, or band, of each of the components forms a cylindrical layer with a maximum concentration along the mean cross section of the layer. The process of separating the mixture into a series of bands on the column is called **development.** The movement of coloured compounds (hence the name chromatography) can be followed visually. The separation of colourless but luminescing substances is observed in the light of a mercury lamp. In all other cases, the lower adsorption zone with the least strongly adsorbed component is allowed to come down (until it eventually emerges from the column), followed

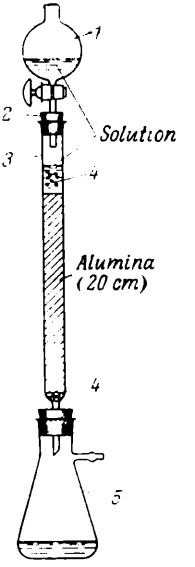


Fig. 1.14.
Apparatus for adsorption chromatography:
1—dropping funnel (100 ml); *2*—rubber stopper; *3*—tube (28 × 1.7 cm); *4*—cotton wool pad; *5*—receiver (250 ml).

by the second adsorption zone with the most strongly adsorbed substance (elution). The elution can be traced by allowing drops of the solution to fall onto a watch glass, which are then evaporated. The pure solvent comes out first, followed by the first component, then again the pure solvent, followed by the second component. Portions of the eluate can be collected automatically into separate vessels and the content of the eluted component can be determined from the refractive index of the solution (by means of the Obreimov flow refractometer).

Substances with different functional groups are arranged in the following series according to their ability to be adsorbed (under the same conditions):

$$RH < ROCH_3 < RNO_2 < RN(CH_3)_2 < R-CO-OCH_3 < RNH-CO-CH_3 < \\ < RNH_2 < ROH < R-CO-NH_2 < R-CO-OH$$

Aromatic hydrocarbons are adsorbed more strongly than fatty saturated compounds (aliphatic hydrocarbons); unsaturated hydrocarbons are adsorbed more strongly than saturated ones.

According to their desorbing (eluting) power, solvents are arranged in a series almost parallel with their dielectric constants (in parentheses): water (81), methanol (31.2), ethanol (25.8), acetone (21.3), ethyl acetate (6.1), ethyl ether (4.4), chloroform (5.2), benzene (2.3), carbon tetrachloride (2.2), cyclohexane (2), petroleum ether (1.9).

Elution is effected by a solvent which stands in the series above the one used first.

Paper Partition Chromatography. The relation between adsorption chromatography just described and partition chromatographic technique can be understood from the diagrams shown in Fig. 1.15*a* and *b*.

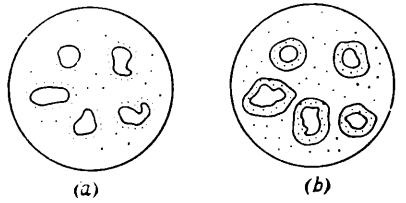


Fig. 1.15.
Column cross-sections:
(*a*) for adsorption chromatography; (*b*) for partition chromatography.

As seen from this figure, in partition chromatography, the grains of the adsorbent have adsorbed one solvent and elution is effected by another solvent immiscible with the first, and the distribution of the substances takes place between these solvents. The modified technique known as paper chromatography constitutes the most important application of partition chromatography. The fibres of paper adsorb water and the substances to be separated are distributed between the water-immiscible solvent and the aqueous layer of paper fibres. We shall confine our consideration to this most important case.

A separation by paper chromatography is achieved as follows. A sheet of special filter paper, say, 20 by 25 cm in size, is gripped between two glass plates so that the narrower edge (20 cm) comes beyond the plate by 3.5 cm. Minute drops (the amount not exceeding 0.005 ml) of the sample solution are placed from a capillary pipette on this edge 2.5 cm from the end of the sheet and 2 cm from each other. Drops of solutions of known substances (standards) are also applied to the paper sheet for comparison. The solvent is then allowed to dry or is evaporated by heating it slightly with an infrared lamp, if required. For uniform moistening to be attained, the paper sheet is bathed in water vapours under a jar and is then placed vertically in a vessel filled at a given temperature with the vapours of the solvent to be used for development. The vessel is then closed. Handbooks on chromatographic techniques specify the kind of solvent most suitable for a particular substance. In any event, the solvent (or a mixture of solvents) to be used for the purpose must be immiscible with water and be saturated with it. The role of the solvent is to extract by fractions and separate the solute from the aqueous phase (adsorbed by the paper) as a result of capillary flow, the water phase being left undissolved. Among the solvents usually employed for paper chromatographic technique are, for example, water-saturated 1-butanol, 2-butanol, 1-hexanol, cyclohexanol, cyclohexanone, phenol, butyl acetate.

Then the bottom end of the sheet (up to the points of solute application) is dipped into a trough with a pool of mixed solvent and water and is allowed to stand in the vessel for several hours (up to 48 hours) until the advancing front of the solvent approaches the top. The sheet is then removed from the vessel and the spots of the adsorbed substances that have ascended the paper by capillary action are made visible by means of a colour reaction. If the spot of the substance being analysed has travelled the same distance as the known substance, this is sufficient for its identification. In the case of complete uniformity of conditions (standard paper, constant temperature, definite solvent specified by the procedure) such an identification can be made by comparing the measured R_f value of the sample spot with the corresponding values given in special handbooks or in original works. The quantity R_f (rate of flow) is defined as the ratio of the distance travelled by the component to the distance travelled by the solvent front for the same time interval and is a characteristic constant of the substance. If necessary (when many substances are to be separated or when the R_f values in a given solvent are similar), two-dimensional partition chromatography is used. In this technique, the sheet of paper treated as indicated above and dried (but not subjected to a colour reaction) is again bathed in water vapours and placed in a vessel, its long side being put on the trough. The trough contains a new solvent also mixed with water. Further

treatment is the same. A chromatogram such as that shown in Fig. 1.16 is obtained in this case.

Paper chromatography is commonly used for identification of substances present in a mixture, but it may also be employed for approximate quantitative determinations, say, photometric determinations—from the colour or the area of spots or by cutting out spots before treatment with a colour reagent (its position can be determined from the position of the neighbouring spot subjected to the action of reagent) and by eluting the test substance from it with a suitable reagent. This sample may then be subjected to any kind of quantitative analysis. The amounts of substances obtained are too small to be used for preparative purposes.

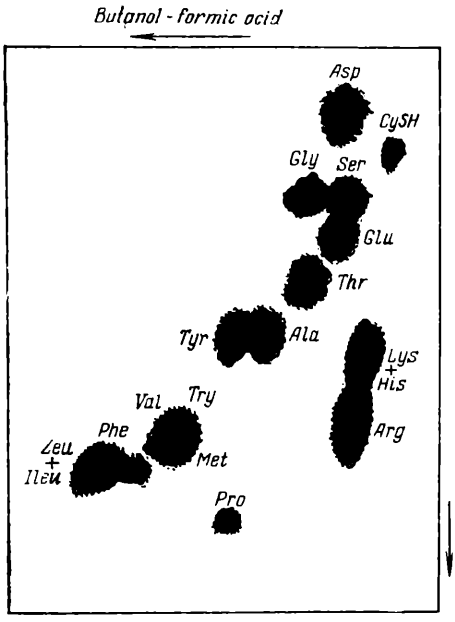


Fig. 1.16.

Two-dimensional chromatogram of a mixture of amino acids after development with ninhydrin.

Thin-Layer Chromatography. An ever increasing importance is attached to thin-layer chromatography proposed by N. A. Izmailov and M. S. Shraiber. This technique may, in principle, be based on adsorption or partition, but usually its adsorption version is employed. It combines the advantages of column chromatography (a wide range of adsorbents, the possibility of use for preparative purposes) and paper chromatography (speed, applicability for analytical purposes). As to the procedure used this type of chromatography bears a closer resemblance to paper chromatography.

An adsorbent (alumina of any grade, kiezelguhr, starch, cellulose, powdered polyamide, etc.) is mixed with a liquid (usually, water) to obtain a slurry, which is spread uniformly on a clean glass plate, about 10 by 20 or 20 by 20 cm, or better in a special chamber of the same size (Fig. 1.17). An excess of slurry (over the desired thickness) is removed with the aid of a roller and the layer is dried in an oven at 100-150°C. This layer (sometimes with an admixture of a binder such as gypsum) is called the fixed layer. More frequently, non-fixed adsorbent layers are used, a cylinder being employed for ramm

ing them to the glass. For analytical purposes, a 0.25-mm layer is spread, and for preparative purposes, a layer from 0.75 to 2 mm. As a guide, 0.001 cm of the test solution is placed from a micropipette on the slurry and is allowed to spread a little, and then various solvents (eluants) are placed in the centre of the spot and the most suitable is chosen. Then an amount of the test solution equal to that used in a preliminary test (containing fractions of a milligram of

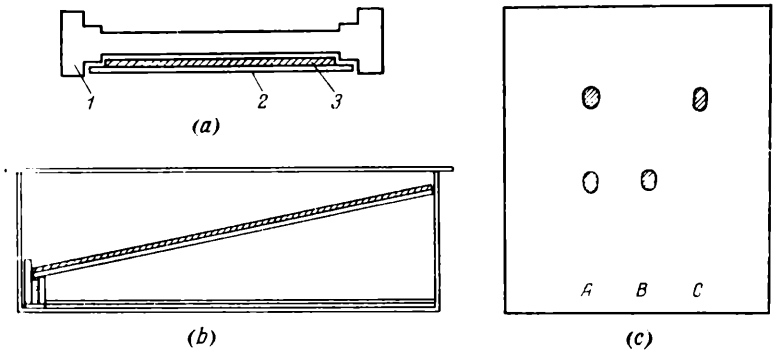


Fig. 1.17.

Apparatus for thin-layer chromatography:

(a) device for spreading a layer of adsorbent; (b) chamber for chromatographing with a solvent (eluant) at the bottom; (c) plate with a separated mixture A of two known substances B and C; *1*—spreader; *2*—plate; *3*—adsorbent.

the substance) is applied to a plate with a fresh layer at a point on a line parallel to one end of the plate, at a distance of 1 cm from it (the starting line); then a known substance is applied as a spot at the same starting line at a distance of about 2 cm from the first point, and the other control substances are placed 2 cm farther along the starting line. The end of the plate near the starting line is dipped to an inclined position into the solvent (eluant) which is at the bottom of a glass chamber, the air in which is saturated with the solvent vapour. The walls of the chamber and its bottom are covered with strips of filter paper. Complete thermostating is not required, but an approximately constant temperature is necessary, for which purpose the chamber is covered with a close-fitting lid. It would be still better if the solvent is applied to the edge of the adsorbent through a capillary slit. After 10-30 min the plate is removed and the eluant dried. This is followed by the development of the invisible spots of the substance, which may have travelled up to 10 cm. If coloured substances are involved, spots are visible and no development is needed. Nor is it required for substances that luminesce in the ultraviolet light. Development is effected with iodine vapours which are soluble in many substances or with a solution of perman-

ganate which gives spots of manganese dioxide, or with any other reagent that gives a colour-producing reaction with test substances. These techniques enable a comparison of the distance travelled by each component of the test mixture with the distance travelled by

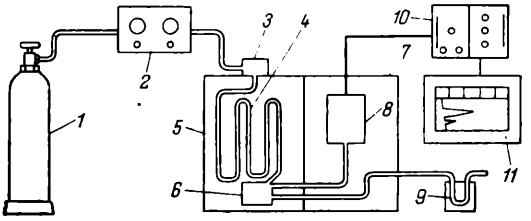


Fig. 1.18.

Diagram of apparatus for gas chromatography (for semipreparative purposes): *1*—cylinder of carrier gas; *2*—pressure regulator and gas-flow regulator; *3*—vessel; *4*—chromatography column; *5*—thermostat; *6*—stream splitter; *7*—thermostat for detector; *8*—detector; *9*—container for collecting fractions of sample; *10*—power supply and detector signal amplifier; *11*—recorder.

known substances and the unknown substances are identified on the basis of the R_f values measured. Development evidently serves only for "visualization" of the spot of the substance to be identified.

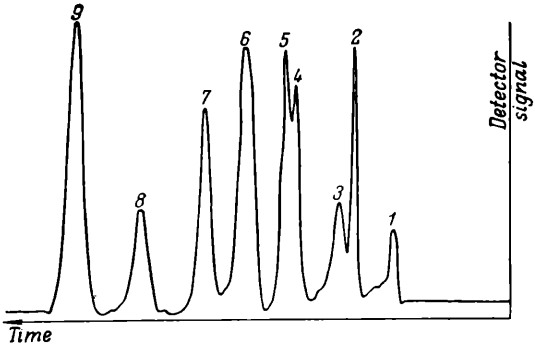


Fig. 1.19.

Chromatogram of a mixture of aldehydes and ketones on celite with 10 per cent of α-hydroxydipropionitrile (50°C); the flow-rate of carrier gas 140 ml/min): *1*—acetaldehyde; *2*—propionaldehyde; *3*—isobutyraldehyde; *4*—acetone; *5*—*n*-butyraldehyde; *6*—isovaleraldehyde; *7*—methyl ethyl ketone; *8*—*n*-valeraldehyde; *9*—methyl *n*-propyl ketone.

When this distance and hence the position of the spot of each component of the mixture has been determined, the corresponding areas of the adsorbent can be separated without development and each component eluted separately.

Thin-layer chromatography is an important tool for every synthesizing chemist in identifying the constituents of the mixture obtained by synthesis.

Gas-Liquid Chromatography. This is a special case of partition chromatography. This technique has become very important in the field of analytical chemistry, but it is more and more adapted to preparative separation of substances. Just as in paper chromatography, the fractionation of substances in gas-liquid chromatography takes place between two phases—the stationary phase and the mobile phase, but an indifferent gas (usually, nitrogen) is used as the mobile phase. The stationary phase used for separation of high-boiling substances may be high-boiling and sufficiently thermally stable solvents—paraffins, low-melting polycyclic aromatic hydrocarbons such as benzyl diphenyl, esters of phthalic acid and, most often, polysiloxanes. For gases or low-boiling substances to be separated, use is made, for example, of formamide. The stationary liquid phase is applied to a solid support—usually kieselguhr (0.5 g of the liquid per 1 g of kieselguhr), porous SiO_2 or ground silicate brick. The apparatus is shown schematically in Fig. 1.18.

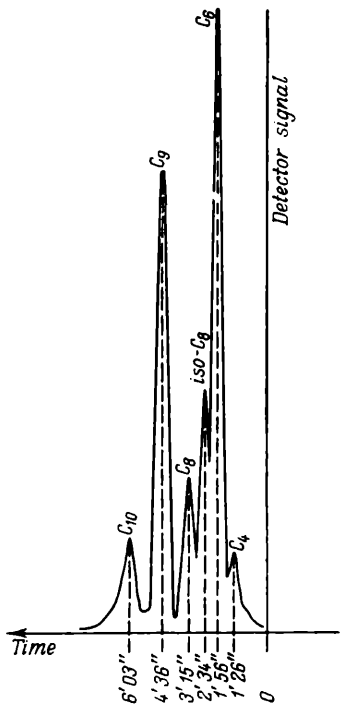


Fig. 1.20.

Chromatogram of a mixture of fatty acids according to thermal conductivity (glass column 2 m long; solid phase—glass; stationary phase—a silicoorganic elastomer; carrier gas—nitrogen; 120°C):

C_4—butyric acid; C_6—caproic acid; C_8—ethylcaproic acid, caprylic acid; C_9—pelargonic acid; C_{10}—capric acid.

A chromatographic column *4* is a long (several tens of centimetres to several metres), thin (4–6 mm) capillary tube filled carefully and uniformly with grains of kieselguhr of the same size, moistened with the stationary liquid phase. The tube is bent so as to be housed in a thermostat *5* which is heated by vapours of a boiling liquid (in other designs, it is heated by a resistance heater). The efficiency of such columns is equivalent to that of distillation columns consisting of hundreds and sometimes even of thousands of theoretical plates.

The mixture to be investigated is introduced into vessel *3*. Then pure nitrogen (argon or helium) is passed through the system. The gases emerging from the column are led into an analyser or detector with automatic recording. Various types of chromatograms are shown in Figs. 1.19 and 1.20.

Time is plotted along the horizontal axis and the concentration of the substance being eluted by nitrogen, along the vertical axis. This concentration is proportional to the magnitude of the detector signal. The total amount of substance can be judged from the area bounded by the peak. With good separation there is no overlap of the peaks. Experiments with known substances enable one to establish the point (or, more correctly, the time) at which a peak appears, which makes it possible to identify the substance. With the aid of analysers one can determine the presence and the amount of impurity being eluted. The substance is either decomposed (for analyses) or not (for preparative purposes). In the first case, the eluate is burned off and the thermal conductivity of nitrogen with an impurity of CO_2 formed is continuously measured, which serves as a measure of the amount of eluate. In the second case, use is also often made of a thermal analyser and either the thermal conductivity or the density of the emerging gas is continuously measured and compared with the density of "pure" nitrogen in a control test. The sensitivity of the method is such that one can determine as little as 0.01-0.001 per cent of the substance in nitrogen.

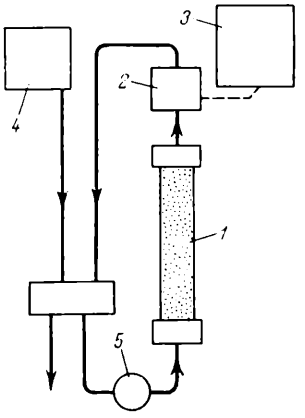


Fig. 1.21.

Diagram of circulation apparatus for gel-chromatography (stream delivered upwards to prevent caking of gel):

1—column; *2*—spectrophotometer in the path of stream; *3*—recorder; *4*—vessel with solvent; *5*—pump.

Gas-liquid chromatography has found extensive application since the fifties of this century and has become one of the most important and principal techniques for separation of small amounts of substances—gases and any other compounds capable of exerting a vapour pressure of a few millimetres of mercury.

Gel Chromatography. A more recent technique for separation of substances and their identification is the use of gels. We shall only briefly discuss the principle of gel chromatography (gel filtration). The apparatus used is shown schematically in Fig. 1.21.

A distinguishing feature of gel chromatography is that the crosslinked macromolecules (see page 378) of gels contain solvent-filled pores of definite molecular size, which are accessible to the smaller of the molecules to be separated. Therefore, in contrast to adsorption chromatography, the first to pass through the column in gel chromatography (and the first to be eluted by the solvent) are the largest molecules, and the last to emerge from the column are the smallest ones. Since pores are of different size, intermediate fractions of the substances are also isolated.

The separating column is filled with grains of a lyophilic or hydrophilic gel. As examples of the former may be cited natural gel-formers—agar, dextrans, say, commercial preparations Sephadex G-25

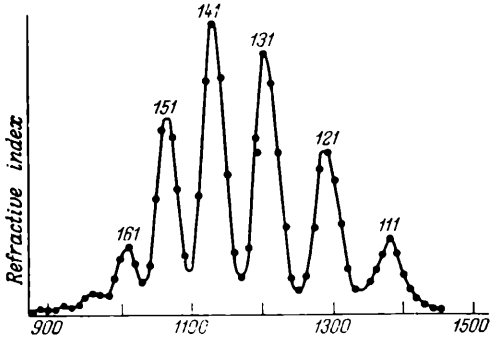


Fig. 1.22.

Gel-chromatogram of a mixture of glucose, cellobiose, and other oligosaccharides, including cellohexaose in aqueous solution on Sephadex G-25.

and G-50 (for dextrans, see Volume II), or synthetic—polyacrylamide, crosslinked polystyrene.

A solution of the substances to be separated is gradually sucked by a pressure pump through the column from bottom to top and the concentration of the solution at the outlet is determined from a physical characteristic, say, by measuring the refractive index, or spectrophotometrically. If necessary, the solution is made to circulate for some time and is then eluted by the solvent.

As an example, a curve is shown in Fig. 1.22 for the gel chromatography of a mixture of glucose and corresponding oligosaccharides (see Volume II), including cellohexaose in aqueous solution on the gel Sephadex G-25. The refractive indices (as indicators of the concentration) are plotted along the ordinate and the volumes of eluting solvents along the abscissa.

1.4. Analysis of Organic Compounds

A. Qualitative Analysis

The detection of organogenetic elements in an organic compound presents no difficulties.

Carbon. When the sample is mixed with an excess of powdered cupric oxide and the mixture is heated, carbon dioxide is formed, which is passed into baryta water [a solution of barium hydroxide, $Ba(OH)_2$] protected against the entrance of CO_2 from the air. The formation of a precipitate of $BaCO_3$ indicates the presence of carbon in the sample.

Hydrogen. Hydrogen is nearly always present in organic compounds and therefore a qualitative test is seldom resorted to for its detection. It can be detected indirectly, when carbon is tested for in a long test tube, the top part of which is externally cooled. If hydrogen is present, water will condense as drops on the colder parts of the test tube, which can be recognized, for example, by the fact that the colourless powder of anhydrous cupric sulphate becomes blue.

Oxygen. Since there are no reliable qualitative tests for detection of oxygen, its presence is deduced from the results of quantitative analysis.

Nitrogen. Nitrogen is most simply determined quantitatively by using a method developed by Dumas (see below). If, however, for some reason or another, a qualitative test is required, nitrogen can be detected by means of the Lossen reaction. To about 0.01 g of a sample of the compound to be analysed in an open test tube there is added about 0.05 g of metallic sodium. Upon completion of the reaction (if a reaction has taken place), the test tube is heated, first carefully and then to redness, regardless of the combustion of sodium. When the combustion is complete, the bottom of the red-heated test tube is dipped into a porcelain dish which contains 3-5 ml of water. The end of the test tube breaks and the melt gets into the water. After the sodium residue has reacted with water, the resulting solution containing sodium cyanide formed by nitrogen is filtered and a drop of a dilute solution of green vitriol is added to it; the solution is then acidified with hydrochloric acid until it shows acid reaction and a drop of a solution of ferric chloride is added to it. The formation of Prussian blue indicates the presence of nitrogen. This test is very sensitive and yields a positive result with many types of nitrogen compounds, but not with all. Easily decomposable aromatic diazo compounds evolve gaseous nitrogen and do not form a cyanide under the conditions described. The qualitative test for nitro-

gen is therefore often replaced by a quantitative determination by the Dumas method (or the Dumas-Pregl method; see below).

Sulphur. The fusion of a sample with sodium (just as described in the test for nitrogen) in the presence of sulphur results in the formation of sodium sulphide which is detected in solution by the nitroprusside reaction or by the reaction with lead or copper(II) salts (formation of a black precipitate).

Use may also be made of the Carius decomposition (see the test for phosphorus) in which sulphur oxidized to sulphuric acid is identified by the formation of a precipitate of barium sulphate.

The Halogens. A thick wire (about 3 mm) of red copper is ignited in the oxidizing flame of a gas burner until the flame ceases to assume a green colour. When the wire cools off, a drop (or a small crystal) of the test substance is applied to its end. When it is introduced into the burner flame, the latter is coloured green due to the formation of volatile copper halide. This is a very sensitive test for Cl, Br and I, but much less sensitive for F. Organic cyanides also give this reaction even in the absence of halogens.

Phosphorus and Other Elements. A drop (or a small crystal) of the test substance is sealed off together with 3-5 drops of fuming nitric acid ($d = 1.52$) in a thick-walled tube of good glass (hard glass is not necessarily required), the end to be sealed off being drawn into a thick-walled capillary. Heat the tube gradually in a special oven to 300-350°C and maintain this temperature for 3-5 hours. Then turn off the oven and let the sample cool off. Remove carefully the tube, wrapping it with a towel (as its end is withdrawn from the oven) so that only the capillary remains unwrapped. Introduce the capillary carefully into the flame of a blowpipe (*wear protective glasses!*). When the capillary glass becomes soft, the gases break through it and handling the tube becomes safe. Make a scratch on the end of the tube with a file, touch the scratch with a hot glass rod; a crack appears and the tube end with a capillary breaks away readily. Dilute the nitric acid solution with water.

When heated in a sealed tube an organic compound burns away completely to form CO_2 and H_2O; phosphorus is converted to phosphoric acid, sulphur to sulphuric acid, and the other elements to the corresponding acids or nitrates. They can be detected by using ordinary methods of qualitative analysis; for example, phosphoric acid is detected by the formation of a yellow precipitate with ammonium molybdate.

II. Quantitative Analysis

Carbon and Hydrogen. The principles of quantitative determination of carbon and hydrogen were worked out by Liebig around 1830. His methods are still applicable at present. More often, however, use

is made of microanalysis based on the same principles and developed by Pregl. The amount of the substance required for microanalysis is 50 times less and is three times faster. A very convenient technique of microanalysis is one devised by M. Korshun and N. Gel man and conducted by combustion in an empty tube.*

The apparatus used for microdetermination of carbon and hydrogen is shown in Fig. 1.23.

From 3 to 5 mg of the substance is weighed out to the nearest 0.002 mg in a long, narrow quartz beaker. The beaker is introduced

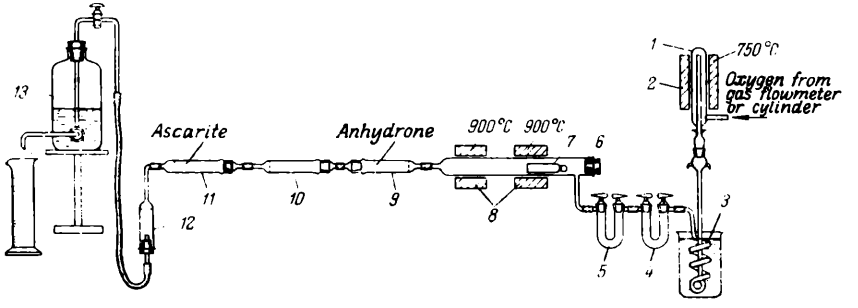


Fig. 1.23.

Schematic representation of combustion train for determination of carbon and hydrogen:

1—platinum catalyst; *2* and *8*—electric furnaces; *3*—coil; *4* and *5*—U-tubes containing Anhydrone and Ascarite to remove H_2O and CO_2 from O_2 stream; *6*—combustion tube; *7*—boat; *9*—weighed absorption tube containing Anhydrone; *10*—weighed absorption tube to absorb oxides of nitrogen; *11*—absorption tube for CO_2; *12*—the last tube preventing back flow of atmospheric CO_2 or H_2O into the apparatus; *13*—aspirator (Mariotte vessel).

into an empty quartz combustion tube *6* and a current of oxygen purified from hydrogen, water and carbon dioxide is gradually (35-50 ml/min) passed for 3 min into an electrical furnace *8* operating at a temperature of 900°C.

Oxygen is purified from hydrogen and organic impurities by passing the gas over a platinum catalyst heated up to 750-800°C. Crude separation of the water formed is effected by condensation in a coil *3* and complete removal of the water and CO_2 is achieved by means of absorption tubes *4* and *5* filled with anhydrous magnesium perchlorate (Anhydrone) and asbestos impregnated with molten sodium hydroxide (Ascarite) in such a way that Anhydrone is the first and last on the pathway travelled by the gas. The gas from the combustion tube is led through a series of three successively connected absorption tubes (which have been weighed on the microbalance): *9*—for water; *10*—for nitrogen oxides; and *11*—for carbon dioxide.

* Korshun, M. O. and N. E. Gelman, *New Methods of Elemental Microanalysis*, Goskhimizdat, 1949; V. A. Klimova, *Principal Micromethods for Analysis of Organic Compounds*, Izd. Khimiya, 1967 (in Russian).

The design of an absorption tube is shown in Fig. 1.24. The first tube (*9*) is filled with Anhydrone (anhydrous magnesium perchlorate), and the third (*11*) with Ascarite. These tubes are weighed and connected immediately before the combustion.

The pressure in the system is regulated by means of an aspirator *13* (the so-called Mariotte vessel).

The process of combustion takes 10 min. It is started with the ignition of the open end of the combustion tube, into which is placed

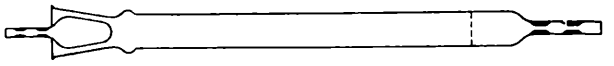


Fig. 1.24.
Pregl absorption tube.

a quartz beaker containing the weighed sample. After the combustion is complete the absorption tubes are blown with air for 2–3 min, removed and weighed carefully on the microbalance. The gain in weight of the first absorbent corresponds to the amount of water, from which the content of hydrogen in the sample is calculated; the gain in weight of the second absorbent *11* gives the amount of carbon dioxide, from which the content of carbon in the sample is deduced.

The calculation is made by means of the formula

$$\% \text{ C} = \frac{f_C \times \text{weight of } CO_2 \times 100}{\text{weight of sample}}$$

$$\% \text{ H} = \frac{f_H \times \text{weight of } H_2O \times 100}{\text{weight of sample}}$$

where $f_C = C/CO_2 = 0.2729$, and $f_H = H/H_2O = 0.1119$.

If the substance to be burned contains halogens and sulphur, an additional absorption tube containing metallic silver in the form of shavings heated in a special furnace is interposed between the combustion tube and the absorption tube for water. The halogens are absorbed when the sample is heated up to 450°C and absorption of sulphur oxides takes place on heating up to 750°C. Figure 1.25 shows a tube for simultaneous determination of carbon, hydrogen, halogens and sulphur.

If the compound contains nitrogen the oxides of nitrogen resulting from the combustion must be oxidized to nitric acid and absorbed, for which purpose after the absorption tube with Anhydrone is put an absorption tube (Fig. 1.26) containing a solution of potassium permanganate in concentrated sulphuric acid (*caution on dissolution!*), followed by another Anhydrone tube and an absorption tube for CO_2 (see Fig. 1.23).

Nitrogen. The determination of nitrogen is carried out by using the Dumas-Pregl method.

A quartz tube filled with copper and wire cuttings of cupric oxide is connected to a micro-azotometer (micro-nitrometer) filled with

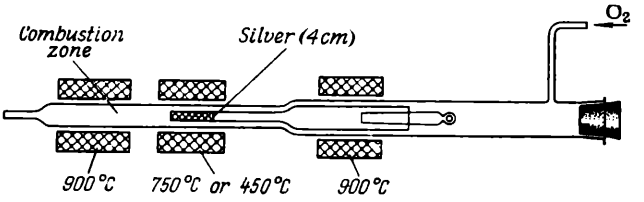


Fig. 1.25.

Combustion tube for simultaneous determination of carbon, hydrogen, halogens and sulphur.

a 40-percent solution of potassium hydroxide (Fig. 1.27). Into the entrance end of the tube is introduced CO_2 from Kipp apparatus loaded with marble boiled in water and diluted with dilute hydrochloric acid. The apparatus must supply pure carbon dioxide, which is checked by the completeness of absorption of CO_2 by the alkali in the micro-nitrometer (the presence of only a small amount of microbubbles which does not practically increase the volume of the gas in the nitrometer is permissible). A weighed sample of the compound (2-3 mg) is placed into the combustion tube which contains a layer of copper and cupric oxide; the sample left on the tube wall is swept with pure powdered cupric oxide and then CO_2 is passed through the tube. The part of the tube with copper oxide is heated in a movable electrical furnace and the issuing gases are conducted into the nitrometer filled up to the mark with potassium hydroxide solution. Then the combustion is started, the furnace being moved to the sample until it covers the sample.

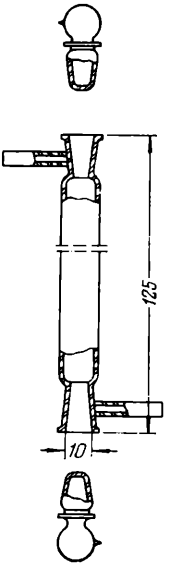


Fig. 1.26.

Absorption tube for oxides of nitrogen.

The layer of metallic copper which is in the exit end of the tube reduces oxides of nitrogen to pure nitrogen.

When the combustion is complete and all the nitrogen is swept into the nitrometer with a current of carbon dioxide, the temperature of the gas in the nitrometer is allowed to even out and then the temperature and atmospheric pressure are recorded and the volume of nitrogen over the potassium hydroxide solution is measured in the

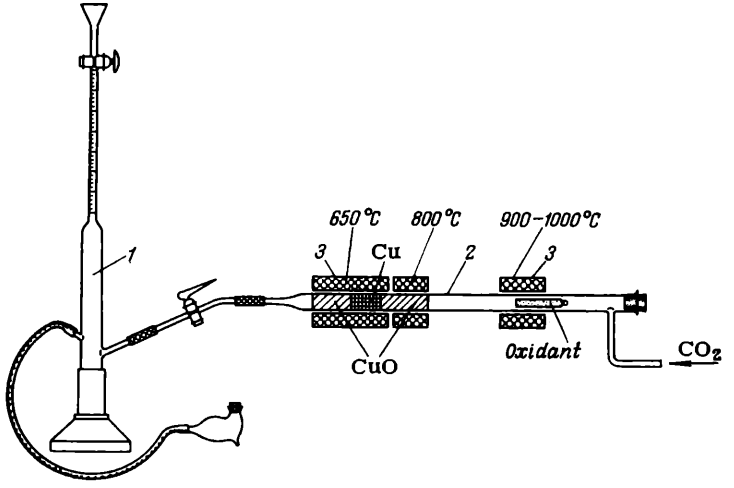


Fig. 1.27.

Microdetermination of nitrogen by the Dumas-Pregl method:
1—nitrometer; *2*—combustion tube; *3*—electric furnaces.

narrow calibrated portion of the nitrometer (no corrections need be introduced for the steam pressure because it is negligible over the 40-percent solution of potassium hydroxide). Since the potassium hydroxide solution wets the walls of the narrow measuring tube of the nitrometer, an empirical correction has to be introduced for this seeming increase of the volume: the measured volume is reduced by 2.0 per cent. The volume of nitrogen thus obtained is corrected to standard conditions of temperature and pressure with the aid of appropriate tables and its weight amount is determined.

Other Elements. We shall consider only briefly the quantitative determination of other organogenetic elements. No satisfactory method has been available for a long time for oxygen and by tradition it is not determined and the amount of oxygen is found by difference after the other elements have been determined. Quanti-

tative determination of oxygen is carried out as follows. A weighed sample of the compound to be analysed is ignited in a quartz tube in a stream of very pure nitrogen and the gases formed are passed through granular carbon black at 1150°C. All the oxygen is converted to carbon monoxide which is oxidized to CO_2 over powdered I_2O_5. Then CO_2 is absorbed by Ascarite in the weighed absorption tube (see page 63).

The halogens and sulphur can be determined by decomposing a sample of the compounds to be analysed (the Carius method). The sample is heated gradually up to 300-350°C with pure nitric acid ($d = 1.52$) in a sealed thick-walled tube. A sample weighing 2 or 3 mg is used for a microdetermination and one or two drops of nitric acid solution are added to it. For a macrodetermination, 0.2-0.3 g of the compound is weighed out and mixed with 2 ml of nitric acid solution. The sample contained in a short test tube is placed in the sealed tube so that it does not come into contact with the nitric acid before the tube is sealed. When halogens are to be determined, a weighed portion of silver nitrate (in a small test tube) is introduced into the tube. The tube is sealed in such a manner that the sealed end is drawn into a thick-walled capillary. The tube is heated gradually in a special furnace up to 300°C and is kept at this temperature for 5-8 hours after which the furnace is turned off. After cooling, the capillary is cautiously introduced into the flame of a blowpipe—when the glass softens the gases break through the capillary. The upper end of the tube is cut off, the contents are washed into a beaker and either the silver halide formed is weighed or the excess of silver nitrate is titrated by one of the known methods. Sulphur is determined by ordinary conventional methods—in the form of sulphate.

C. Derivation of Empirical Formulas

The results of a quantitative analysis are expressed by the percentage content of a given element in the compound being analysed. To convert the percentage ratios to the relative atomic proportions, one must divide the percentage content of each of the elements by the atomic weight of the element concerned and then divide the series of the values obtained by the smallest one. It is these numbers that will express the minimum possible number of atoms in the molecule.

Example. In an analysis for urea, the following percentage contents of the elements were determined (with an accuracy of 0.2 per cent): carbon—19.93 per cent; hydrogen—6.62 per cent; nitrogen—46.70 per cent (totalling 73.25 per cent); oxygen—26.75 per cent (by difference).

We divide each of the above values by the atomic weight of the element it represents:

carbon = 19.93 : 12 = 1.66
nitrogen = 46.70 : 14 = 3.33
hydrogen = 6.62 : 1 = 6.62*
oxygen = 26.75 : 16 = 1.66

Dividing the values obtained by the smallest value (1.66), we get:

carbon = 1.66 : 1.66 = 1
nitrogen = 3.33 : 1.66 = 2
hydrogen = 6.62 : 1.66 = 3.98
oxygen = 1.66 : 1.66 = 1

Thus, on the basis of this analysis the empirical formula of urea can be expressed as $C_1H_4O_1N_2$ (since a molecule cannot contain a fractional part of an atom) or as $C_2H_8O_2N_4$.

In order to determine the molecular formula of urea, i.e., a formula that tells us how many atoms of each kind are present in its molecule, one has to know its molecular weight. Having determined the molecular weight of urea by one of the methods just described (and found it to be equal to 60), of all the possible multiple empirical formulas we choose the first molecular formula, namely, CH_4ON_2.

D. Determination of Molecular Weight

The molecular weights of organic compounds are but seldom determined by the methods based on the Avogadro-Gerhardt law. Use is commonly made of the ebullioscopic and cryoscopic methods based on Raoult's law which is known, just as the Avogadro-Gerhardt law, from a course of general chemistry.

In the cryoscopic method, a weighed portion of a substance, p, is dissolved in a weighed portion P of one of the solvents used for this purpose, more often benzene or glacial acetic acid. The weight of the substance is chosen so that there is 0.05-0.02 g of the test substance per 100 g of the solvent. A Beckmann cryoscopic apparatus (cryoscope) (Fig. 1.28) is used, which is equipped with a Beckmann thermometer (Fig. 1.29) with scale divisions of 0.01°C. This thermometer is used to determine first the freezing point of the pure solvent and then the freezing point of a solution of the test substance in that solvent. The lowering of the freezing point of the solution is directly proportional to the number of molecules of the substance dissolved in a given mass of solvent.

* The calculation is simplified here by assuming the atomic weight of hydrogen (1.008) to equal unity.

Knowing the lowering of the freezing point of the solution prepared by dissolution of 1 mole of any known substance in 1000 g of the solvent used, we can calculate the molecular weight of the

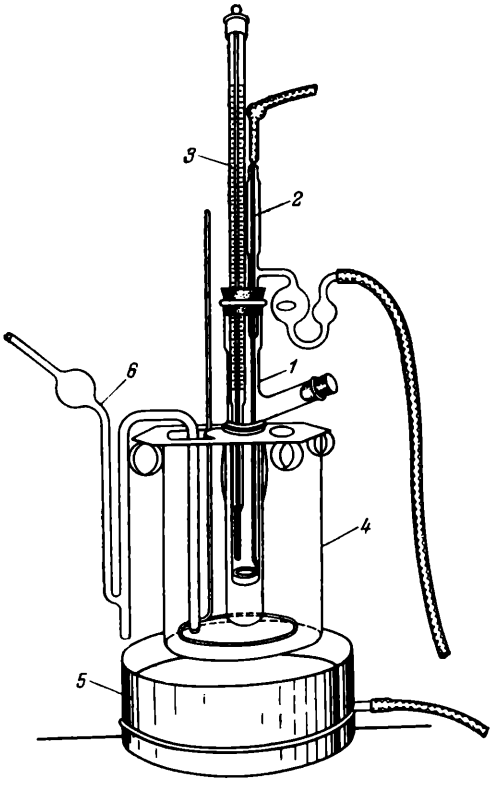


Fig. 1.28.

Beckmann cryoscopic apparatus:

1—freezing tube; *2*—stirrer; *3*—Beckmann thermometer; *4*—thermostat; *5*—bath; *6*—heat regulator.

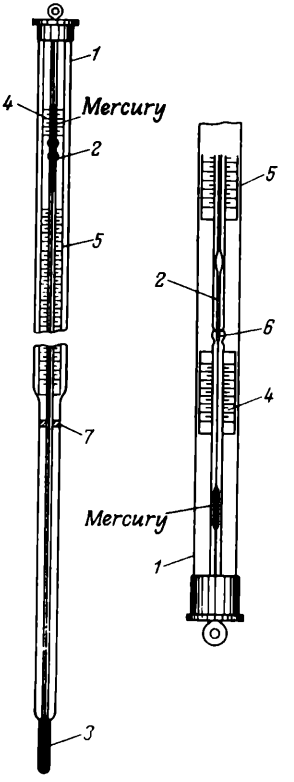


Fig. 1.29.

Beckmann thermometer:

1—additional reservoir; *2*—capillary; *3*—thermometer bulb; *4*—subsidiary scale; *5*—main scale calibrated for temperature intervals of 0.01°C per engraved scale division; *6*—capillary tip from which mercury flows; *7*—cork padding packing. (The amount of mercury filling the capillary between the end of main scale and the capillary tip is equivalent to the mercury column corresponding to 7°C).

solute. This cryoscopic constant K which is identical for solutions of all substances in a given solvent is termed the *molecular depression* of the solvent concerned; it is an extrapolated quantity since the cryoscopic method involves more dilute solutions.

Thus, the molecular weight M of a compound is calculated from the formula:

$$M = K \frac{1000p}{P\Delta t^\circ}$$

where Δt° is the observed lowering of the freezing point of the solution as compared with the freezing point of the solvent.

The values of K for some solvents are as follows:

Water	1.86
Acetic acid (glacial)	3.90
Benzene	5.07
Phenol	7.2
Camphor	40

The extremely high molecular depression of camphor led Rast to propose a simplified cryoscopic method which is widely employed at the present time. The Rast cryoscopic method requires neither a cryoscope nor a Beckmann thermometer; only an ordinary thermometer with scale divisions of 0.1°C is needed. In this method, a weighed portion of the substance to be analysed (p) is cautiously melted, mixed thoroughly with a weighed portion, P, of camphor and the mixture is fused and the fused mass is allowed to solidify. Just as in melting-point determinations, a capillary is filled with the powdered fused mass and is attached to the bulb of the thermometer, and the melting point (which is equal to the freezing point) of the fused mass is determined. Using the same thermometer, one can determine the melting point of pure camphor (178.6°C). The difference in the melting points, Δt°, is included in the formula for determination of molecular weight, which now assumes the following form:

$$M = 40 \cdot \frac{1000p}{P\Delta t^\circ}$$

where p and P are expressed in grams.

The only inconvenience of the exceedingly simple and rapid Rast method is the high melting point of camphor, which precludes its application for the determination of substances which are readily decomposable or highly volatile at that temperature. If the molecular weights of such substances are to be determined, use may be made of another solvent with a high cryoscopic constant. Such are, for example, cyclohexanol (m.p. 24.7°C, $K = 42.5$), camphene (m.p. 49°C, $K = 31$). Camphene, however, is an unsaturated compound and one must make certain that the test substance does not react with it.

In the ebullioscopic method, the boiling point of a pure solvent is measured with the aid of a thermometer with scale divisions of

0.01°C. Then a weighed portion of the test substance, p, is introduced into a definite amount of solvent, P, and the elevation of the boiling point of the solution, $\Delta t°$, is measured. The law that governs the elevation of the boiling point of the solution is the same as for the lowering of the freezing point of the solution, and the formula used to calculate molecular weight is analogous:

$$M = K_{eb} \frac{1000p}{P\Delta t°}$$

The ebullioscopic constants K_{eb} for the most widely used solvents are as follows:

Water	0.51
Benzene	2.61
Ethyl ether	2.16
Chloroform	359

The two methods based on Raoult's law become inaccurate as the molecular weight of solute increases. For substances of ordinary molecular weight, i.e., a molecular weight equal to several tens or hundreds, the accuracy of determination is 5 to 10 per cent, which is sufficient for reliable selection of a molecular formula from a series of empirical formulas. The explanation is simple. The amount of freezing-point lowering (or boiling-point elevation) becomes less and less for a solution of the same weight concentration, whereas the influence of invariably present impurities with relatively smaller molecular weights increases.

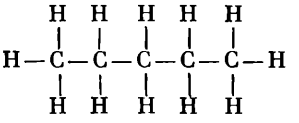
The methods described above cannot be applied to high-molecular-weight compounds (polymers), whose molecular weights are many thousands or tens of thousands. In this case, the following three methods are used: viscometric, osmotic and ultracentrifuge (sedimentation) methods, which in their turn cannot be applied to substances of ordinary molecular weight.

1.5. Classification of Organic Compounds

Organic compounds are classified according to their structure, this classification being based on the character of the carbon skeleton of hydrocarbons, i.e., the sequence of carbon atoms linked to one another. Compounds that contain atoms other than carbon are regarded as derivatives of hydrocarbons, in which hydrogen atoms are replaced by such atoms called heteroatoms. An exception is made for such structures in which the heteroatom closes the chain of carbon atoms into a ring. Such cyclic or ring compounds are classified as a special class of compounds termed **heterocycles.**

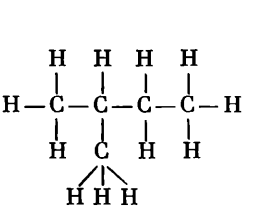
All organic compounds are primarily divided into two large groups: **acyclic compounds**—with an open chain and **cyclic compounds**—with a closed chain.

Acyclic compounds are also called fatty or aliphatic (from a Greek word meaning fat) since fats and fatty acids belong to this class. These compounds may have a "normal" structure, i.e., have an unbranched skeleton similar to the skeleton of normal pentane

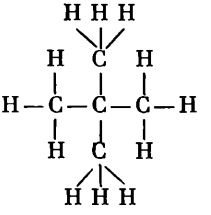


n-Pentane

or a branched skeleton (with various degrees of branching), such as isopentane and neopentane:



Isopentane

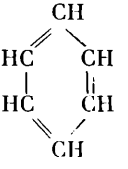


Neopentane

A subclass of fatty or aliphatic compounds is formed by unsaturated fatty compounds—the isologues of the previous saturated compounds. They are characterized by the presence, in the chain of carbon atoms, of one or more double or triple bonds between adjacent carbon atoms.

Cyclic compounds are classed into **isocyclic,** in which there is a cyclic grouping consisting of several carbon atoms closed into a ring, and **heterocyclic,** in which the ring includes one or more atoms other than carbon (heteroatoms). Heterocyclic as well as isocyclic compounds may be unsaturated, in which case they contain double or triple carbon-carbon bonds. A special position among such compounds is occupied by so-called **aromatic compounds**—six-membered rings containing alternating three single and three double carbon-carbon bonds or bonds between a carbon atom and a heteroatom.

The parent and most important aromatic compound is benzene



Aromatic compounds also include five-membered rings which contain two double bonds and an atom (carbon or heteroatom) carrying two free electrons. This classification is largely formal since substances of all the classes are more or less readily converted to one another.

Sometimes the principal relations, say, of a heterocyclic compound lead to acyclic rather than to heterocyclic compounds. Therefore, the sequence of presentation of the material in this book will deviate from the strict classification scheme adopted in handbooks of organic chemistry.

ACYCLIC COMPOUNDS

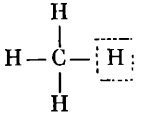
Chapter 2

Saturated Compounds

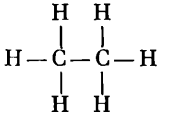
2.1. Alkanes

The simplest member of this series is **methane**, CH_4. All other hydrocarbons that are classified as alkanes (or paraffins) are members of the **homologous series of methane**, and since each homologue differs from its immediate neighbours by a CH_2 unit (a methylene group), the composition of all alkanes may be represented by the general formula C_nH_{2n+2}, where n is an integer. Monovalent groups of radicals (i.e., mentally isolated parts of the molecule) which result from the paraffins by the removal of one hydrogen atom are known under the general name of **alkyl** groups. They are described by the general formula C_nH_{2n+1}. The name of each individual group is obtained from that of the corresponding saturated hydrocarbon by changing the end syllable *-ane* into *-yl*. Thus, CH_4 is meth*ane*, and CH_3— is meth*yl*. Divalent and trivalent radicals are also known. By the removal of successive atoms of hydrogen from methane we may derive the following: *methylene*, CH_2, and *methine*, CH.

The next member of the homologous series is **ethane**, C_2H_6. Its structure can be derived from the structure of methane by substitution of one methyl group for one hydrogen atom:



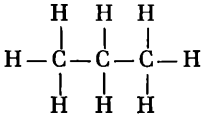
Methane



Ethane

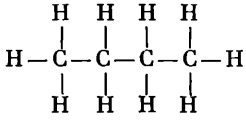
The structure of each other homologue can be derived from the preceding one by means of the same operation—by substitution of a methyl group (or radical) for a hydrogen atom in the preceding

member. In this way, we obtain **propane**, C_3H_8, from ethane:

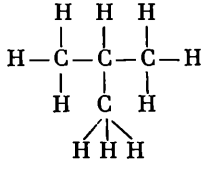


Propane

If we wish to apply the same operation to propane, we shall notice that, in contrast to the replacement of hydrogen atoms in methane and ethane, in this case it is important which of the eight hydrogen atoms is substituted by a new methyl group. Whereas in methane and ethane all the hydrogen atoms enter into the composition of methyl groups and are identical, in propane only six extreme hydrogen atoms participate in the structure of methyl groups, while the other two, central hydrogen atoms are contained in the methylene radical. If one of the six extreme hydrogen atoms is replaced by a methyl group, butane (C_4H_{10}) will result, which has an unbranched, or normal, chain of carbon atoms—a "normal skeleton". But if one of the two hydrogen atoms in the methylene group is replaced by a methyl group, the chain will become branched and a hydrocarbon of the same composition will result—isobutane, C_4H_{10}, which is isomeric with *n*-butane but differs from it by its properties.



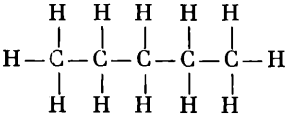
n-Butane



Isobutane

Beginning with butane, as the number of carbon atoms increases, the number of isomers possible increases steeply so that an alkane containing ten carbon atoms can have one of 75 isomeric structures.

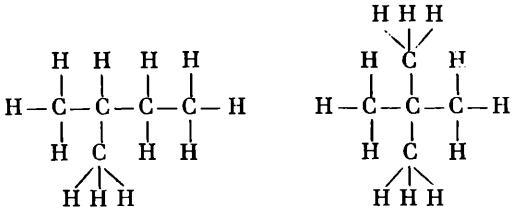
n-Butane (normal butane) contains two kinds of hydrogen atom—six hydrogens belonging to the methyl groups and four hydrogens of the methylene groups. Substitution of a methyl group for one of the hydrogen atoms of the methyl groups results in *n*-pentane, C_5H_{12}:



n-Pentane

If one of the methylenic hydrogen atoms of *n*-butane is replaced by a methyl group, isopentane is formed, which is an isomer of *n*-pentane.

A third pentane isomeric with the two preceding ones, namely neopentane, can be obtained from isobutane by substituting a methyl group for the hydrogen of the methine group:



Isopentane Neopentane

It can easily be seen that the parent isobutane has two kinds of hydrogen atom: one hydrogen atom of the methine group which has just been replaced, and nine hydrogen atoms of the methyl groups. If we replace one of them by a new methyl group, no other isomer of pentane will be formed—it simply does not exist. The structure thus obtained will again be that of isopentane.

Thus, the branching of the homologous series is such that the branches coincide occasionally. A similar replacement of one of the equivalent hydrogen atoms in each isomeric pentane may lead, identical structures being cancelled, to five hexane isomers. The beginning student must train himself in deriving all possible structures for pentanes, hexanes, and heptanes.

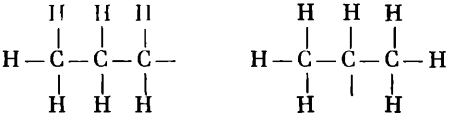
The number of structural isomers increases with the number of carbon atoms of the skeleton, as can be seen from Table 2.1. The number of structural isomers predicted by the structure theory is invariably justified by experiment.

TABLE 2.1 **The Number of Isomers in the Alkane Series**

Formula	Name	Number of isomers	Formula	Name	Number of isomers
CH_4	Methane	1	$C_{12}H_{26}$	Dodecane	355
C_2H_6	Ethane	1	$C_{13}H_{28}$	Tridecane	802
C_3H_8	Propane	1	$C_{14}H_{30}$	Tetradecane	1858
C_4H_{10}	Butane	2	$C_{15}H_{32}$	Pentadecane	4347
C_5H_{12}	Pentane	3	$C_{20}H_{42}$	Eicosane	366, 319
C_6H_{14}	Hexane	5	$C_{25}H_{52}$	Pentacosane	36, 797, 588
C_7H_{16}	Heptane	9	$C_{30}H_{62}$	Triacontane	4, 111, 846,
C_8H_{18}	Octane	18			763
C_9H_{20}	Nonane	35	$C_{40}H_{82}$	Tetracontane	62, 491, 178,
$C_{10}H_{22}$	Decane	75			805, 831
$C_{11}H_{24}$	Undecane	159			

When a carbon atom is combined in such a manner that only one of its four valencies is satisfied by carbon (as, for example, the carbon of a methyl group in the hydrocarbons just described), it is called a **primary carbon atom.** If two valencies are linked to carbon, the atom under consideration is known as **secondary** (the carbon atom of a methylene group in our examples). A **tertiary carbon atom** is one bonded to three carbons (e.g., the carbon of the methine group in isobutane). Finally, an example of a **quaternary carbon atom** with all four valencies linked to carbon atoms is the central carbon of neopentane.

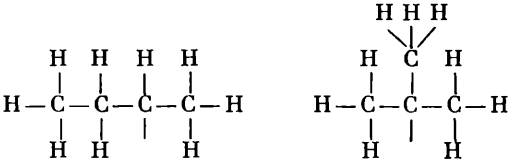
It should be noted that radicals may also be structurally isomeric. Examples are normal propyl and isopropyl (secondary propyl):



n-Propyl *sec*-Propyl

which have the same skeleton and differ in the position of the hydrogen atom being replaced.

Radicals differing in the carbon skeleton are exemplified by the following:



Secondary normal butyl Tertiary butyl

Table 2.2 gives some of the physical properties of the members of the homologous series of normal hydrocarbons, and Table 2.3 presents the physical properties of all the isomers of butane, pentane, hexane, and heptane.

The property that varies most regularly in the homologous series of methane is the boiling point. As the series is ascended, beginning with pentane (the first hydrocarbon in the series which is liquid at room temperature), each additional CH_2 group corresponds to a rise of 25-30°C in boiling point; this difference gradually falls off and at the 18th member of the series it becomes as small as 13°C, etc. The change from the liquid to the gaseous state is counteracted by the weak forces of mutual attraction between the atoms of the various molecules. The greater the number of atoms in each molecule and the nearer their atoms approach each other, the stronger is this attraction. The first factor (the number of atoms) is reflected in the regular increase of the boiling points of straight-chain homologues,

TABLE 2.2. Normal Hydrocarbons

Formula	Name	Melting point, °C	Boiling point, °C	Density d_4^{20}	Refractive index n_D^{20}
CH_4	Methane	−184.0	−161.5	0.4150 (at −164 °C)	—
C_2H_6	Ethane	−172.0	−88.3	0.5610 (at −100 °C)	—
C_3H_8	Propane	−189.9	−42.17	0.5853 (at −44.5 °C)	1.2898
C_4H_{10}	Butane	−135.0	−0.5	0.5788	1.3326
C_5H_{12}	Pentane	−131.6	36.2	0.6260	1.3570 (at 16 °C)
C_6H_{14}	Hexane	−94.3	69.0	0.6603	1.3750
C_7H_{16}	Heptane	−90.5	98.4	0.6838	1.3876
C_8H_{18}	Octane	−56.5	125.8	0.7036	1.3975
C_9H_{20}	Nonane	−53.7	150.8	0.7176	1.4054
$C_{10}H_{22}$	Decane	−30 to −32	174.0	0.7301	1.4120
$C_{11}H_{24}$	Undecane	−26.5	195.8	0.7410	1.4184
$C_{12}H_{26}$	Dodecane	− 9.6	214.5	0.7487	1.4216
$C_{13}H_{28}$	Tridecane	−6.2	234.0	0.7568	1.4419 (at 17° C)
$C_{14}H_{30}$	Tetradecane	5.5	252.5	0.7650	1.4459
$C_{15}H_{32}$	Pentadecane	10.0	270.5	0.7689	1.4315
$C_{16}H_{34}$	Hexadecane	20.0	287.5	0.7751	1.4345
$C_{17}H_{36}$	Heptadecane	22.5	303.0	0.7780	1.4370
$C_{18}H_{38}$	Octadecane	28.0	317.0	0.7768 (at 28° C)	1.4349 (at 35° C)
$C_{19}H_{40}$	Nonadecane	32.0	330.0	0.7770 (at 32° C)	1.4360 (at 35° C)
$C_{20}H_{42}$	Eicosane	36.8	205.0 (at 15 mm Hg)	0.7780 (at 37° C)	1.4340 (at 43° C)

and the second, in the difference in the boiling points of isomeric hydrocarbons (Table 2.3). Normal or straight-chain hydrocarbons whose molecules pack together in the liquid phase most strongly have the highest boiling point and density, and the most highly branched-chain hydrocarbons have the lowest boiling point and density (compare, for example, neopentane with normal pentane and isopentane).

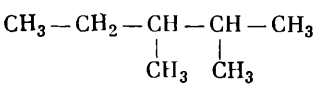
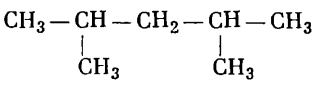
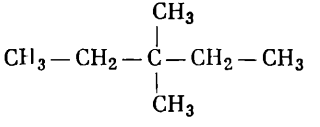
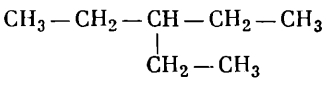
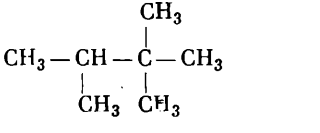
The melting points of the straight-chain members of the homologous series rise gradually. Thus, n-$C_{15}H_{32}$ melts at 10°C, n-$C_{20}H_{42}$ at 36.8°C, and n-$C_{100}H_{202}$ does so at 115°C. The melting-point curve

TABLE 2.3. **Alkanes***

Formula	Name	Melting point, °C	Boiling point, °C	Density d_4^{20}	Refractive index n_D^{20}
CH_4	Methane	—184	—161.5	0.4150 (at —164°C)	—
CH_3-CH_3	Ethane	—172	—88.3	0.5610 (at —100°C)	—
$CH_3-CH_2-CH_3$	Propane	—189.9	—42.17	0.5853 (at —44.5°C)	1.2898
$CH_3-CH_2-CH_2-CH_3$	*n*-Butane	—135.0	—0.5	0.5789	1.3326
$(CH_3)_2CH-CH_3$	Isobutane	—145.0	—10.2	0.6030 (at 0°C)	—
$CH_3-CH_2-CH_2-CH_2-CH_3$	*n*-Pentane	—131.6	+36.2	0.6260	1.3570 (at 16°C)
$(CH_3)_2CH-CH_2-CH_3$	Isopentane	—160.5	28.0	0.6197	1.3550
$(CH_3)_2C(CH_3)_2$	Neopentane	—20	9.5	0.5910	1.3476 (at 0°C)

$CH_3-CH_2-CH_2-CH(CH_3)-CH_3$	2-Methylpentane	—153.7	60.0	0.6540	1.3720
$CH_3-CH_2-CH(CH_3)-CH_2-CH_3$	3-Methylpentane	—	64.0	0.6760 (at 15°C)	1.3765
$CH_3-CH_2-C(CH_3)_2-CH_3$	2,2-Dimethylbutane	—98.2	49.7	0.6487	1.3675
$CH_3-CH(CH_3)-CH(CH_3)-CH_3$	2,3-Dimethylbutane	—135.1	58.1	0.6680 (at 17°C)	1.3783
$CH_3-(CH_2)_5-CH_3$	*n*-Heptane	—90.5	98.4	0.6838	1.3876
$CH_3-CH_2-CH_2-CH_2-CH(CH_3)-CH_3$	2-Methylhexane	—119.1	90.0	0.6789	1.3848
$CH_3-CH_2-CH_2-CH(CH_3)-CH_2-CH_3$	3-Methylhexane	—119.4	91.85	0.6871	1.3886
$CH_3-CH_2-CH_2-C(CH_3)_2-CH_3$	2,2-Dimethylpentane	—125.0	79.2	0.6738	1.3821

Table 2.3 (continued)

Formula	Name	Melting point, °C	Boiling point, °C	Density d_4^{20}	Refractive index n_D^{20}
	2,3-Dimethylpentane	—	89.8	0.6951	1.3920
	2,4-Dimethylpentane	—123.4; —119.2	80.5	0.6727	1.3814
	3,3-Dimethylpentane	—134.5	86.0	0.6933	1.3909
	3-Ethylpentane	—94.5	93.5	0.6982	1.3934
	2,2,3-Trimethylbutane	—25.0	80.9	0.6901	1.3894

(see Fig. 2.1) shows that the melting point increases with an alternating and gradually decreasing difference.

Solid alkanes are crystalline. The factors influencing the boiling point tell less on the melting point since on melting the van der Waals forces are weakened but insignificantly. The melting point which reflects the strength of intermolecular forces in a crystal is

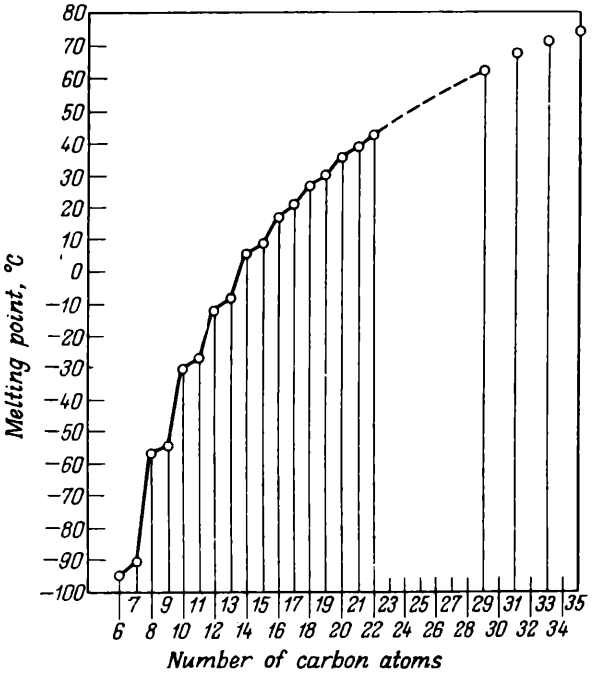


Fig. 2.1.

The melting point of normal paraffinic hydrocarbons versus the number of carbon atoms in the molecule.

more strongly affected by the geometrical factors of molecular packing in the crystal lattice. The more symmetrically built is the molecule, the more readily and firmly it is packed into a crystal and the higher is its melting point. For example, symmetrically built neopentane melts at —20°C, while linear *n*-pentane melts at 131.6°C. The temperature region of stability of the liquid phase is the narrowest for branched-chain symmetrical structures of the neopentane type.

In the case of paraffinic hydrocarbons with a very long chain of carbon atoms, say, polyethylene which results from the polymerization of ethylene and which is a mixture of high-molecular-weight

homologues of methane with a molecular weight of more than 10,000, although melting is possible (the melting point varies from 105 to 125°C for various polyethylenes), van der Waals forces hold molecules together so firmly in the molten state that it is easier to break the chemical bond in a chain of carbon atoms than to overcome the intermolecular forces. Therefore, on heating in a vacuum the substance decomposes without being converted to the vapour.

Although the carbon chain of normal saturated hydrocarbons is written in a straight line for convenience, it must be remembered that the carbon atoms are arranged in a zig-zag pattern in the molecule, just as in any other carbon chain. Later in this book we shall consider the stereochemical proof of the so-called *tetrahedral configuration of the carbon atom*, formulated by van't Hoff (1871), and confirmed as early as the first quarter of this century by studies of the X-ray diffraction by crystals of organic compounds.

The carbon atom in saturated compounds holds four identical atoms [for example, the hydrogen atoms in methane, CH_4, or the carbon atoms in *n*-pentane, $C(CH_3)_4$] in such a manner that the directions from the central carbon atom to the atoms attached to it lie along the axes of a regular tetrahedron (Fig. 2.2). It is the centre of this tetrahedron which is occupied by the central carbon atom C. The angle between the tetrahedral bonds is 109°28′. If the carbon atom holds four different atoms, the angles are somewhat (a little) changed and the tetrahedron ceases to be regular, but the situation does not change in principle. From X-ray studies it is also known that the distance between the centres of carbon atoms linked to each other in saturated compounds is 1.54 Å; the distance from the centre of the carbon atom to that of the hydrogen atom is 1.1 Å.

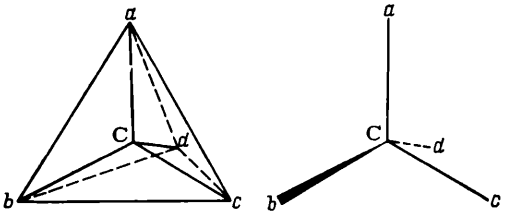
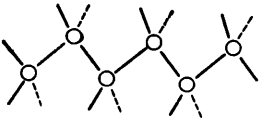
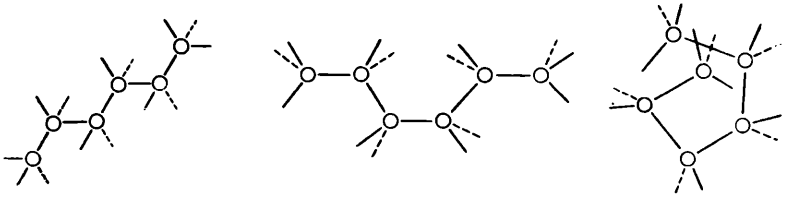


Fig. 2.2.
Model of the tetrahedral carbon atom.

Thus, the normal chain of a paraffinic hydrocarbon must be as follows



Since, however, the rotation around the carbon-carbon bond is unhindered and requires almost no energy, it follows that such rotations allow the carbon chain to assume the various rotational arrangements or **conformations** (for example, *a*, *b*, and *c*):



(*a*) (*b*) (*c*)

Most often the chain of carbon atoms assumes conformation (*a*) which has the lowest energy. The presence of branchings or substituents can change the conformation of the chain.

Conformations can easily change into one another; they all correspond to one and the same chemical entity.

Paraffinic hydrocarbons of normal structure crystallize together with urea from alcoholic or acetone solutions in the form of **clathrates*** —crystalline compounds in which the molecules of a hydrocarbon fill the hexahedral cavities formed by the molecules of urea in the crystal. The chains of normal paraffins consisting of at least six carbon atoms enter these cavities. The molecules of branched-chain hydrocarbons cannot be accommodated by these cavities and therefore form no such crystalline compounds with urea. This makes it possible, with the aid of urea, to separate compounds with a normal chain of carbon atoms (not only hydrocarbons but also a number of their derivatives) from branched-chain or cyclic compounds.

A. Occurrence of Alkanes in Nature

Alkanes, along with the hydrocarbons of other series (cycloalkanes and aromatic hydrocarbons), enter into the composition of petroleum (crude oil). The lower gaseous alkanes—methane, ethane, and propane—are the constituents of natural gas, the major portion of which (up to 98 per cent) is methane. The same gaseous hydrocarbons are found dissolved in petroleum. Methane found in coal mines is known as **firedamp** or **mine gas.** The putrefaction of cellulose in the absence of air also gives rise to methane which is liberated in swamps (**marsh gas**). The distillation of petroleum gives products

* Derived from the Latin word *clathratus* meaning enclosed or protected by cross bars of a grating.— *Tr.*

TABLE 2.4. **The Group Hydrocarbon Composition of Fractions of Crude Oils Boiling at Temperatures up to 300°C**

Mangyshlak crude oil — paraffin-base, tarry, low-sulphur content; *Ozeksuat crude oil* — paraffin-base, low sulphur content, low tar content; *Romashkino crude oil* — high-sulphur content, high tar content, paraffin-rich; *Ust'-Balyk crude oil* — high-sulphur content, high tar content, paraffin-rich; *Markovo crude oil* — sulphur-bearing, low tar content, paraffin-rich; *Surakhany crude oil* (naphthene-base) — low tar content, low sulphur content.

Hydrocarbon	Composition, per cent								
	Mangyshlak		Northern Caucasus	Tatar ASSR	Siberia			Baku	
	Zheltybai	Uzen'	Ozeksuat	Romashkino	Ust'-Balyk	Sosnin	Markovo	Surakhany	Kalin
Aromatic	11.15	44.53	14.83	18.77	8.0*	12.0*	13.0*	8.6	18.72
Naphthenic	—	—	23.98	25.48	28.0	36.0	16.0	61.20	41.83
Paraffinic	88.85	55.47	61.17	55.75	64.0	52.0	71.0	30.20	39.45

which are mixtures of hydrocarbons enriched more or less with alkanes. Such are petroleum ether (boils between 40 and 75°C), gasoline or petrol (70-120°C), kerosene (150-300°C), fuel oil, lubricating oil, vaseline, paraffin wax.

The petroleum found in the Northern Caucasus (Grozny) and in Mangyshlak is rich in paraffins. The group compositions of the various kinds of petroleum found in the USSR are listed in Table 2.4. Solid, relatively high-boiling paraffins occur in the form of deposits of so-called **ozokerite** (ozocerite). Purified ozocerite known as **ceresine** is utilized in the same areas as paraffin wax. Finally, paraffins can also be isolated from the products of dry distillation of coals and peat.

Methane and the hydrocarbons contained in crude oils play a very important role in national economy, being used, along with coal, as the principal source of energy and of organic raw materials for the chemical industry. Especially large quantities of hydrocarbon mixtures in the form of petroleum fractions are used as motor fuels for automobiles and aircraft equipped with piston engines (gasoline) and also for jet aircraft and rockets (kerosene).

B. Preparation of Alkanes

Industrial Methods. Apart from the distillation of petroleum, use is also made of the following industrial methods for the production of mixtures of hydrocarbons.

1. *Hydrogenation of coal* (Bergius process). Powdered coal is mixed with the high-boiling hydrocarbon oil from the distillation of the hydrogenation product of the previous portion of coal, and the resulting mixture is treated with hydrogen at a temperature of 450-500°C and a pressure of 200-300 kg/cm^3 in the presence of iron as a catalyst. The liquid hydrogenation product is distilled to obtain gases, gasoline and heavier fractions (cuts); the heaviest fractions are subjected to additional destructive hydrogenation. In this way, gasoline, lubricating oils and raw materials for chemical synthesis were produced in Germany where there are no natural resources of petroleum.

2. *Synthesis from carbon monoxide* (F. Fischer and H. Tropsch). When a mixture of carbon monoxide and hydrogen (known as *water gas* or *synthesis gas*) is passed at 200°C and atmospheric pressure over a catalyst (metallic iron and cobalt), a mixture of hydrocarbons is produced, which includes synthol consisting mainly of normal paraffins with an impurity of olefins:

$$n\mathrm{CO} + (2n+1)\mathrm{H_2} \xrightarrow{\text{catalyst}} \mathrm{C}_n\mathrm{H}_{2n+2} + \mathrm{H_2O}$$

Synthol serves as a raw material for organic synthesis and for production of motor fuels.

3. *Cracking of petroleum* (see page 92). In the cracking of crude oil, the higher alkanes (and the other hydrocarbons contained in petroleum) are broken down to a mixture of lower alkanes, beginning with methane, and olefins which are of special importance:

$$C_nH_{2n+2} \longrightarrow C_mH_{2m+2} + C_{n-m}H_{2(n-m)}$$

Thus, cracking is one of the most important methods for industrial production of alkanes (mixed with olefins). Of the alkanes derived from petroleum, propane, butane, isobutane and also isopentane are especially valuable as raw materials for the chemical industry.

Laboratory Syntheses. *Synthesis of methane.* 1. The action of water on aluminium carbide:

$$Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4$$

2. Synthesis of methane from carbon disulphide according to Berthelot (this synthesis is of historical importance):

$$CS_2 + 2H_2S + 8Cu \xrightarrow{\text{heat}} CH_4 + 4Cu_2S$$

3. The heating of sodium acetate with alkali (decarboxylation of acetic acid):

$$CH_3-\overset{\overset{O}{\|}}{C}-ONa + NaOH \longrightarrow CH_4 + Na_2CO_3$$

Synthesis of ethane. 1. The Wurtz reaction proceeds as follows:

$$2CH_3Cl + 2Na \longrightarrow C_2H_6 + 2NaCl$$

2. Kolbe synthesis is the electrolysis of acetates. In this process, the anion CH_3COO^- is discharged at the anode to form the unstable uncharged radical $CH_3COO\cdot$, which decomposes into CO_2 and ethane:

$$2CH_3COO\cdot \longrightarrow C_2H_6 + 2CO_2$$

This method may also be employed for synthesizing other alkanes with an even number of carbon atoms if the starting materials are homologues of acetic acid.

Synthesis of higher alkanes. 1. Reduction of the various derivatives of alkanes—halogen-substituted derivatives, alcohols, acids—by hydriodic acid at a high temperature:

$$CH_3-CH_2-CH_2-CH_2-CH_2Cl + 2HI \longrightarrow$$
$$\longrightarrow CH_3-CH_2-CH_2-CH_2-CH_3 + HCl + I_2$$

2. The action of water on the organometallic compounds of Li, Na, Mg, Zn:

$$C_nH_{2n+1}Br + Mg \longrightarrow C_nH_{2n+1}MgBr$$
$$C_nH_{2n+1}MgBr + H_2O \longrightarrow C_nH_{2n+2} + MgBrOH$$

3. Preparation of alkanes of the general formula C_nH_{2n+2} from olefins C_nH_{2n} (for more detail, see under "Olefins", page 335).

C. Chemical Properties of Alkanes

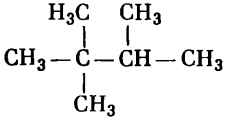
The alkanes were called paraffins (from the Latin words *parum affinittatis* meaning *devoid of affinity*) because of their chemical inertness. They are incapable of adding hydrogen (hence the name saturated hydrocarbons) and entering into uninitiated (see below) reaction with chlorine and bromine (let alone iodine) and are not oxidized in the cold by strong oxidizing agents such as permanganate and chromic acid. The most inert paraffins are methane and ethane.

1. *High-temperature oxidation.* The flame oxidation leads to the complete combustion of all alkanes to carbon dioxide and water. This reaction is most widely used for fuel rather than for chemical purposes. Such a combustion takes place in engines of all types. The oxidation begins even at preflame temperatures and proceeds by the mechanism of chain reactions (see Volume IV under "Free Radicals").

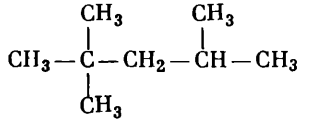
At the first stage of oxidation of a hydrocarbon RH there are formed unstable intermediate products—hydroperoxides ROOH which decompose to form aldehydes, ketones, alcohols, acids, and also free radicals R · which exist for a very short time in the reaction zone.

In an internal combustion engine, when the gasoline vapour and air mixture is compressed, normal hydrocarbons form peroxides which give rise to engine "knock"—uneven combustion of the fuel-and-air mixture after sparking, with resulting loss of power and damage to the piston and cylinder.

Branched paraffins burn more smoothly. Especially valuable as a motor fuel are hydrocarbons with a neostructure, i.e., those having a quaternary carbon atom, and in particular, hydrocarbons with a structure of the "isooctane" type:



2,2,3-Trimethylbutane



2,2,4-Trimethylpentane (isooctane)

Isooctane serves as a reference standard for an arbitrary scale used to evaluate motor fuels by **octane numbers**. The octane-number

scale is based on a value of zero for normal heptane and of 100 for isooctane (Table 2.5).

TABLE 2.5. **Octane Numbers of Selected Alkanes**

Hydrocarbon	Octane number	Blending octane number *	Hydrocarbon	Octane number	Blending octane number *
n-Butane	92	110	2,2,3-Trimethylbutane	104	115
n-Pentane	62	87	2,2,3,3-Tetramethylpentane	125	—
n-Hexane	26 (45)	65	*n*-Nonane	−44	—
n-Heptane	0	52	*n*-Decane	−53	—
n-Octane	−17 (−20)	35	Cyclohexane	77	90
2,3-Dimethylhexane	79	—			
2,2,4-Trimethylpentane or isooctane	100	113			

* Blending octane numbers have been extrapolated from the behaviour of blends. Some hydrocarbons in a pure form show a lower octane number than that extrapolated from their behaviour in blends.

Gasoline (petrol) is compared with a mixture consisting of a per cent of isooctane and $(100-a)$ per cent of *n*-heptane. If the behaviour of both samples in an engine is the same, gasoline is assigned the octane number a. The octane number varies somewhat in tests carried out with the use of poor and rich mixtures with air. In the latter case the octane number is lower.

The performance of gasoline used for piston engines in old types of aircraft and automobiles is improved by addition of synthetic hydrocarbons such as isooctane (for preparation of these hydrocarbons from olefins, see page 341). The octane number can be further raised by the addition of small amounts of antiknock compounds. The most commonly used antiknock compound is a mixture of tetraethyl lead, $Pb(C_2H_5)_4$, and ethylene dibromide, which is known as **ethyl fluid.** Ethyl gasolines, however, are highly poisonous. Organometallic manganese-containing antiknock compounds have recently been discovered, which are more effective than ethyl fluid. Gasolines with such additives are not poisonous.

In diesel and rocket engines, where the ability of the fuel to ignite rapidly is essential, the reverse is observed: the most efficient fuels consist of normal hydrocarbons. On the arbitrary rating scale of **cetane numbers**, *n*-hexadecane (cetane): $n\text{-}C_{16}H_{34}$, is given a value of 100, 1-methylnaphthalene being assigned a value of zero. Since

synthol consists largely of unbranched hydrocarbons, its highest-boiling fraction, **kogasin**, is a valuable diesel fuel.

2. *Low-temperature oxidation by oxygen.* At a low temperature, with manganese salts being used as a catalyst, there takes place the oxidation of alkanes in the liquid phase, which also proceeds through the stage of peroxide formation. In this process, the chains of carbon atoms are ruptured and a mixture of saturated acids and hydroxy acids is formed. The process is used on a large scale for oxidation of paraffins and for the manufacture of detergents and surface-active substances.

At higher temperatures, alkanes can be oxidized in the gaseous phase to a mixture of oxygen-containing products—aldehydes, ketones, acids. The reaction is initiated by addition of radical-like molecules with an unpaired electron, say, NO. In this way acetic acid, CH_3COOH, can be produced from butane, and formaldehyde, HCHO, from methane.

3. *Reaction with water.* At a high temperature, over a catalyst (chromic oxide and nickel supported by aluminium oxide), methane reacts with water vapour according to the equation:

$$CH_4 + H_2O \longrightarrow CO + 3H_2$$

Based on this reaction is an important method for the chemical utilization of methane since the resulting gaseous mixture is used for industrial synthesis of methanol, CH_3OH, and serves as a source of hydrogen, say, in the production of ammonia.

4. *Cracking of alkanes.* Methane is the most thermally stable alkane. This is due to the fact that the C—H bond formation energy (98.5 kcal) is considerably higher than the energy of formation of the C—C bond (81 kcal). Moreover, and this is evidently more important, the longer the chain of atoms the more probable is the chance cumulation of energy at any point in the chain. Therefore, higher paraffins are thermally less stable; they undergo thermal decomposition (cracking) even at a temperature of about 450°C. Methane undergoes thermal cracking at a temperature higher than 1400°C according to the equation:

$$2CH_4 \longrightarrow C_2H_2 + 3H_2 \qquad \Delta H = +95_{kcal}$$

This is an endothermic reaction. It forms the basis of one of the methods of industrial production of acetylene.

Ethane when heated to 600-800°C is converted to ethylene:

$$C_2H_6 \longrightarrow C_2H_4 + H_2$$

The reaction probably involves the rupture of the carbon chain with the formation of two methyl groups, the loss of a hydrogen atom by the methyl groups and the union of the methylene groups formed into ethylene.

The fragmentation of large hydrocarbons into smaller ones takes place at random points in the chain and the hydrogen atoms are redistributed among the fragments (radicals) so that a mixture of equimolecular amounts of alkanes and olefins is formed. For example,

$$CH_3(CH_2)_4CH_3 \begin{cases} \longrightarrow CH_3 + CH_2CH_2CH_2CH_2CH_3 \longrightarrow CH_4 + CH_2{=}CH-CH_2CH_2CH_3 \\ \longrightarrow CH_3CH_2 + CH_2CH_2CH_2CH_3 \begin{cases} \longrightarrow C_2H_6 + CH_2{=}CH-CH_2CH_3 \\ \longrightarrow CH_2{=}CH_2 + CH_3CH_2CH_2CH_3 \end{cases} \\ \longrightarrow CH_3CH_2CH_2 + CH_2CH_2CH_3 \longrightarrow CH_3CH_2CH_3 + CH_2{=}CHCH_3 \end{cases}$$

The cracking of heavy fractions of petroleum on a large industrial scale is used to produce olefin-rich fractions of lower molecular weight—gasolines with high octane numbers and gaseous hydrocarbons, among which olefins are especially valuable from the viewpoint of chemical utilization. Two basic cracking processes have been developed, thermal and catalytic. Thermal cracking (pyrolysis) is accomplished by passing petroleum products through pipe stills at 600-750°C and different pressures.

The action of solid aluminium chloride on the mixture even when heated to a relatively low temperature breaks the carbon chains, the higher paraffins being converted, just as at a high temperature, into a mixture of lower paraffins and olefins. The high-temperature cracking also involves the cyclization of paraffins into more stable cycloalkanes and particularly stable aromatic hydrocarbons.

Catalytic cracking over silica-alumina catalysts ($SiO_2 + Al_2O_3$), which was introduced into practice by Houdry (USA, 1934) and is finding an ever increasing application, provides a higher yield of low-boiling fractions than thermal cracking, the gasoline produced being of exceptionally high antiknock quality (up to 80). The catalysts are natural or synthetic silica-alumina used at a temperature of the order of 500°C. Silica-alumina catalysts act as acidic catalysts under such conditions.

The mechanisms of the two cracking processes are different: thermal cracking proceeds by a homolytic mechanism (see page 32) with the rupture of the chain into free radicals, while catalytic cracking occurs by a heterolytic mechanism, with the formation of ions (not shown in the above scheme). This accounts for the different ratios of individual hydrocarbons in the products of thermal and catalytic cracking processes.

5. *Halogenation.* Unexcited chlorine and bromine do not react with alkanes. But if chlorine and bromine are exposed to ultraviolet light (in which case the halogen molecule is broken up into atoms), hydrogen is substituted by halogen. This substitution reaction was given the name of **metalepsy** by Dumas who discovered it in 1834. The final results of chlorination of methane may be expressed by

a series of equations:

$$CH_4 + Cl_2 \longrightarrow \underset{\text{Methyl chloride}}{CH_3Cl} + HCl$$

$$CH_4 + 3Cl_2 \longrightarrow \underset{\text{Chloroform}}{CHCl_3} + 3HCl$$

$$CH_4 + 2Cl_2 \longrightarrow \underset{\text{Methylene chloride}}{CH_2Cl_2} + 2HCl$$

$$CH_4 + 4Cl_2 \longrightarrow \underset{\text{Carbon tetrachloride}}{CCl_4} + 4HCl$$

The role of a free halogen atom and the chain mechanism of the reaction are discussed in Sec. 2.2. At this point we shall only give preliminary information concerning the chain reaction mechanism:

$$\underset{\text{(photolysis of chlorine molecule)}}{Cl_2 \longrightarrow 2Cl\cdot}$$

$$CH_4 + Cl\cdot \longrightarrow CH_3\cdot + HCl$$

$$CH_3\cdot + Cl_2 \longrightarrow CH_3Cl + Cl\cdot$$

The atomic chlorine obtained as the result of the photolysis of molecular chlorine, in contrast to the latter, reacts with methane, abstracting hydrogen with the formation of HCl. The free radical formed—a methyl group—is a highly reactive particle, which upon encounter with a chlorine molecule abstracts one chlorine atom, forming methyl chloride. The second free chlorine atom left again reacts with methane, and so on.

Chlorination of methane is carried out on an industrial scale, particularly for the manufacture of carbon tetrachloride.

Alkanes are all subjected to chlorination (and bromination), chlorine being introduced at the various points in the molecule. Lower alkanes (up to C_3H_8) can be completely chlorinated (up to C_3Cl_8); the higher alkanes are ruptured in the reaction across the carbon-carbon bond (*chlorinolysis*):

$$\rangle C - C \langle + Cl_2 \longrightarrow \rangle CCl + ClC \langle$$

Attempts to iodinate saturated hydrocarbons have so far failed. Direct fluorination of these compounds can be effected by the action of fluorine evolved upon electrolysis at the cathode, or through fluorination with the aid of CoF_3 which gives up one fluorine atom.

6. *Nitration*. At temperatures about 500°C methane can be nitrated by the action of nitric acid and also of nitrogen dioxide. This reaction may be expressed by the following overall equation:

$$CH_4 + HNO_3 \longrightarrow CH_3NO_2 + H_2O$$

The resulting nitromethane finds application in the synthesis of explosive substances and also as a solvent. Under these conditions

the reaction of ethane may take two different courses:

$$CH_3-CH_3+HNO_3-\begin{cases}\longrightarrow CH_3CH_2NO_2\\ \longrightarrow 2CH_3NO_2\end{cases}$$

In the nitration reaction suggested by Konovalov (dilute HNO_3, 140°C), the hydrogen atom attached to a secondary or, notably, to a tertiary carbon atom is replaced by a nitro group (NO_2) much more readily than the hydrogen linked to a primary carbon atom. For example, isopentane forms nitroisopentane:

$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_3+HNO_3 \longrightarrow CH_3-\underset{\displaystyle NO_2}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CH_2-CH_3$$

No such selectivity is observed in the high-temperature nitration (above 400°C) in the gaseous phase.

On an industrial scale, the gasoline fractions are nitrated by nitrogen dioxide in the gaseous phase, the breaking of hydrocarbon chains giving rise mainly to nitromethane, nitroethane, and nitropropanes.

7. *Sulphonation*. When heated a solution of sulphuric anhydride in sulphuric acid (oleum) gradually sulphonates paraffins containing a methine group:

$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_3+H_2SO_4 \longrightarrow CH_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle SO_3H}{\overset{|}{C}}}}-CH_2-CH_3$$

8. *Sulphochlorination*. Under the influence of ultraviolet light, alkanes enter into a substitution reaction with a mixture of excess sulphurous anhydride and chlorine. On an industrial scale, this reaction is used for sulphochlorination of kogasin (a high-boiling fraction of synthol; see page 91). The reaction proceeds by a chain mechanism, being initiated by the chlorine atom resulting from the photolysis of a chlorine molecule. The mechanism of the sulphochlorination reaction may be represented by the following scheme:

$$Cl_2 \xrightarrow{\text{photolysis}} 2Cl\cdot$$

$$C_nH_{2n+2}+Cl\cdot \longrightarrow C_nH_{2n+1}\cdot + HCl$$

$$C_nH_{2n+1}\cdot + SO_2 \longrightarrow C_nH_{2n+1}-\underset{\displaystyle O}{\overset{\displaystyle O}{\overset{\|}{\underset{\|}{S}}}}\cdot$$

$$C_nH_{2n+1}-\underset{\displaystyle O}{\overset{\displaystyle O}{\overset{\|}{\underset{\|}{S}}}}\cdot + Cl_2 \longrightarrow C_nH_{2n+1}-\underset{\displaystyle O}{\overset{\displaystyle O}{\overset{\|}{\underset{\|}{S}}}}-Cl+Cl\cdot \quad \text{and so on}$$

The reaction again gives rise to a chlorine atom which initiates a new step of the chain reaction. Thus, it might seem that one light quantum responsible for the generation of the first pair of chlorine atoms would be sufficient for the entire portion of the alkane to react as a result of such a chain reaction. As a matter of fact, a reaction chain cannot be infinite but involves only a few (tens, seldom hundreds) recurring steps since random encounters of chain-propagating active particles ($Cl\cdot$ or $C_nH_{2n+1}\cdot$ or $C_nH_{2n+1}SO_2\cdot$) will terminate the chain. Such random encounters may be exemplified by the following:

$$C_nH_{2n+1}\cdot + Cl\cdot \longrightarrow C_nH_{2n+1}Cl$$

or

$$C_nH_{2n+1}SO_2\cdot + C_nH_{2n+1}\cdot \longrightarrow C_nH_{2n+1}-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-C_nH_{2n+1}$$

Sulphochlorides derived from kogasin are used for producing detergents.

9. *Catalytic dehydrogenation of alkanes.* At a temperature of 500-600°C paraffins, which are passed in the form of a gas or vapour over chromic oxide, lose two hydrogen atoms and are converted into olefins (A. A. Balandin):

$$C_nH_{2n+2} \xrightarrow{Cr_2O_3} C_nH_{2n} + H_2$$

This reaction is an important industrial process (in the manufacture of synthetic rubbers, page 365).

D Nomenclature of Alkanes

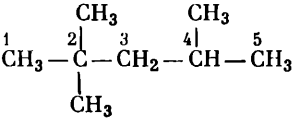
We have seen that the names of the straight-chain members of the homologous series of methane (see Table 2.1), beginning with pentane, are derived from the Greek numerals (to denote the number of carbon atoms) with the ending *-ane* to classify the compound as a paraffin hydrocarbon. To denote isomers, trivial names are prefixed with *iso-*, *neo-*, etc. According to this nomenclature the name of a hydrocarbon, say, pentane, is extended to its isomers which are thus called pentanes. It is easy to see that with increasing number of isomers it would be impossible to devise a different prefix for each of the isomers and some other system of naming is needed.

In 1892, the International Congress at Geneva adopted a new system of nomenclature. The main principle of this nomenclature is as follows. To any particular name there must correspond only one compound and, conversely, a compound of given structure must be represented by only one name which would quickly convey to the reader the structure of the molecule.

For normal hydrocarbons, the Geneva nomenclature adopted their trivial names. For branched hydrocarbons, the longest continuous chain of carbon atoms (the main or principal chain) is selected as the basis for the name which is built according to the number of carbon atoms in this chain, and the branching alkyl groups are regarded as substituent radicals and their names are placed before the names of the respective hydrocarbons. To indicate the position of substituent groups in the main chain, the carbon atoms in the chain are numbered consecutively from one end in such a way as to give the carbon to which the side branch (substituent) is attached as low a number as possible; the number of the carbon atom is written before the name of the respective substituent.

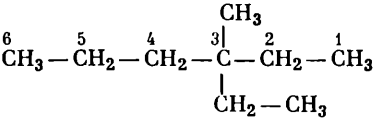
If the side branch starts at a carbon atom equidistant from both ends of the main chain, the numbering is done from the end closest to the "senior radical", i.e., a radical which has a simpler structure. For example, methyl is senior to ethyl, ethyl to propyl, and propyl to isopropyl, etc.

Thus the name of isooctane according to the Geneva nomenclature will be 2,2,4-trimethylpentane:

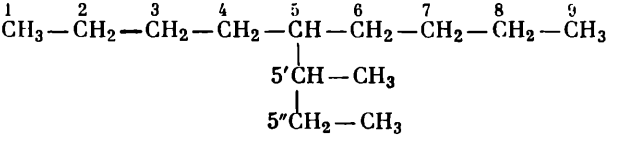


Methyl groups whose carbon atoms are designated by the numerals 1 and 5 are included in the main chain.

The name of the following hydrocarbon is 3-methyl-3-ethylhexane:



If there are substituent radicals in the side chain, the carbon atoms of this chain are numbered, starting with the carbon atom attached to the main chain, which is given the same number as that of the atom of the main chain that carries the branch, but supplied with a prime: 5′, 5″, etc.



According to the Geneva nomenclature, the side-chain substituents are denoted by the prefixes *metho-* (for methyl), *etho-* (for ethyl),

propo- (for propyl), etc. For example, the above hydrocarbon should be named 5-(5′-methopropyl)-nonane.

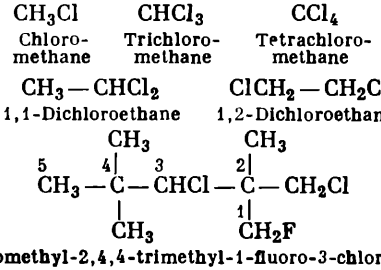
The Geneva nomenclature, however, turned out to be unusual and cumbersome, especially in the case of compounds with functional groups in side chains. In 1957, a new nomenclature was recommended by the International Union of Pure and Applied Chemistry (IUPAC), which does not impose strict limitations on the names of organic compounds. It permits of trivial names for the simplest radicals (isopropyl, *sec*-butyl, etc.). For example, according to the IUPAC rules the above hydrocarbon may be named 5-*sec*-butylnonane.

2.2. Halogen Derivatives of Saturated Hydrocarbons

Compounds that have the structure of alkanes in which one or more hydrogen atoms are replaced by a halogen are called halogen derivatives of alkanes or alkyl halides. Examples are the derivatives of methane mentioned above—methyl chloride, CH_3Cl, methylene chloride, CH_2Cl_2, chloroform, $CHCl_3$ (which might be called methine chloride according to this nomenclature), carbon tetrachloride, CCl_4; the derivatives of ethane—ethyl chloride, $CH_3—CH_2Cl$, ethylidene chloride, $CH_3—CHCl_2$, ethylene chloride, $ClCH_2—CH_2Cl$, which is isomeric with the last-named compound; hexachloroethane, $CCl_3—CCl_3$. The nomenclature given (except for the names of chloroform and hexachloroethane) originated from the theory of radicals—the names are formed from the name of the hydrocarbon radical attached to chlorine. The name of a complex compound cannot be built in this way.

According to the Geneva nomenclature, for the halogen derivatives of alkanes the Geneva name of a hydrocarbon is preceded by the prefixes *fluoro-*, *chloro-*, *bromo-*, or *iodo-* with addition of *di-*, *tri-*, *tetra-*, *penta-*, etc., depending on the number of halogen atoms in the molecule. The position of the halogen is indicated, as before, by the number of the carbon atom to which the halogen is attached.

What has just been said may be illustrated by some examples:



A. Preparation of Halogen Derivatives

Fluorine Derivatives. After 1940 the chemistry of fluorine derivatives began to develop rapidly.

The fluorination by free fluorine leads to the complete destruction of the hydrocarbon molecule:

$$C_nH_{2n+2} + (6n+2)F_2 \longrightarrow nCF_4 + (2n+2)HF$$

If the amount of fluorine is not sufficient, the resulting carbon is in the form of carbon black.

Strong dilution of fluorine with an inert gas makes it possible to accomplish a substitution reaction; but the most efficient methods of fluorination of hydrocarbons are those described below.

1. The action of CoF_3. A hydrocarbon is passed through a tube filled with CoF_3 and heated to a temperature higher than 200°C. The compound CoF_3 is reduced to CoF_2, giving up the fluorine for the replacement of hydrogen and its removal in the form of HF.

2. Electrolysis of acid potassium fluoride, KF·HF, with a carbon anode in the presence of a hydrocarbon to be fluorinated. Fluorination of the hydrocarbon proceeds at the anode.

The two methods can be mainly employed for the preparation of polyfluoroalkanes, up to perfluoroalkanes, i.e., those in which all the hydrogen atoms are replaced by fluorine. In this way it is possible to fluorinate even lubricating oils, whose chain contains several tens of carbon atoms.

Monofluorine and fluorine derivatives with the specified position of fluorine in the chain are produced from chlorine, bromine, and iodine derivatives by means of the halogen exchange reaction. The best starting substances used for preparing monofluorine derivatives are iodine derivatives which are reacted with silver fluoride. To exchange two or more halogen atoms at one carbon atom for fluorine, use is made of chlorine derivatives and antimony trifluoride.

Difluorine derivatives with two fluorine atoms at one carbon atom can be prepared from ketones by the reaction:

$$\begin{matrix} R \\ \diagdown \\ \quad C=O \\ \diagup \\ R \end{matrix} + SF_4 \longrightarrow \begin{matrix} R \\ \diagdown \\ \quad CF_2 \\ \diagup \\ R \end{matrix} + SOF_2$$

1,1,1-Trifluoroderivatives are made by the action of sulphur tetrafluoride on carboxylic acids:

$$RCOOH + 2SF_4 \longrightarrow RCF_3 + 2SOF_2 + HF$$

Chlorine and Bromine Derivatives. The reactions of chlorination and bromination of alkanes by a free halogen in sunlight has already been considered briefly on page 92. What remains here is to discuss the mechanism of this reaction. The action of sunlight, which is

necessary for this reaction to take place, consists in that it causes the halogen molecule to break down into two atoms. Only atomic chlorine is capable of attacking the inert molecule of an alkane and abstracting a hydrogen atom from it:

$$Cl\cdot + C_nH_{2n+2} \longrightarrow HCl + C_nH_{2n+1}\cdot$$

The free radical $C_nH_{2n+1}\cdot$ upon encounter with a chlorine molecule abstracts one atom, leaving the other atom free:

$$C_nH_{2n+1}\cdot + Cl_2 \longrightarrow C_nH_{2n+1}Cl + Cl\cdot$$

This chlorine atom starts a new reaction step similar to the first one. The reaction chain consisting of such steps continues until it is terminated by some accidental factor.

Thus, the ordinary equation of a reaction of the type

$$C_nH_{2n+2} + Cl_2 \longrightarrow C_nH_{2n+1}Cl + HCl$$

reflecting the exact stoichiometry of the reaction, provides no information on the mechanism of the reaction.

The reaction of chlorination (and the more so of bromination) of alkanes is used rather seldom in practice.* It is never used in the laboratory for preparative syntheses because there are more convenient methods for producing individual halogen derivatives.

An inconvenience of the halogen-substitution reaction as applied to alkanes with three or more carbon atoms in the chain is that a mixture of isomers is obtained.

Iodine Derivatives (Alkyl Iodides). Direct iodination of alkanes is infeasible. Iodine derivatives with one iodine atom (alkyl iodides or monoiodoalkanes) are best prepared by the exchange reaction between the corresponding chlorine derivative and sodium iodide in an acetone solution (Finkelstein):

$$RCl + NaI \longrightarrow RI + NaCl$$

Sodium iodide dissolves in acetone, whereas sodium chloride does not.

Other Methods of Synthesis of Halogen Derivatives. Since in the methods of synthesis of halogen derivatives (haloalkanes) described below use is made of classes of compounds not yet discussed in this book, we shall give only a brief review of the methods in the form of general equations. These reactions will be considered in more detail in describing the chemical properties of the starting compounds involved.

* On an industrial scale the reaction is employed only for the chlorination of methane to produce carbon tetrachloride (tetrachloromethane), chloroform (trichloromethane), methyl chloride, methylene chloride, and, to a limited extent, for the chlorination of the pentane fraction of gasoline, which is subject to further hydrolysis to amyl alcohol.

1. Synthesis from alcohols:

$$ROH + HX \longrightarrow RX + H_2O$$
$$3ROH + PBr_3 \text{ (or } PI_3) \longrightarrow 3RBr + P(OH)_3$$
$$ROH + PCl_5 \text{ (or } PBr_5) \longrightarrow RCl + HCl + POCl_3$$

where R = radical C_nH_{2n+1}; and X = Cl, Br, I.

2. Synthesis from carbonyl compounds (aldehydes and ketones):

$$R-\overset{\overset{O}{\|}}{C}-R' + PCl_5 \longrightarrow R-\overset{\overset{Cl\ \ Cl}{\diagdown\ \ \diagup}}{C}-R' + POCl_3$$

where R′ = H or alkyl.

3. Synthesis from olefins:

$$C_nH_{2n} + HX \longrightarrow C_nH_{2n+1}X \qquad C_nH_{2n} + X_2 \longrightarrow C_nH_{2n}X_2$$

4. Synthesis from carboxylic acids:

$$R-\overset{\overset{O}{\|}}{C}-OAg + Br_2 \longrightarrow RBr + CO_2 + AgBr$$

The reaction with chlorine proceeds in an analogous way.

B. Physical Properties of Halogen Derivatives

The physical properties of some of the halogen derivatives are listed in Table 2.6. From the data given it is seen that the introduction of a halogen increases the density (specific gravity) of the compound; polyiododerivatives such as CH_2I_2, CHI_3, CI_4 are organic compounds having the highest density. Liquid methylene iodide, CH_2I_2, is therefore used in mineralogy for determination of the density of minerals. The homologous difference in the boiling points of alkyl halides with the same halogen for the members of the series C_3-C_6 is about 30°C, i.e., almost the same as for the alkanes themselves. Alkyl iodides of the member C_6 boil approximately 30°C higher than alkyl bromides, and the latter boil 25°C higher than the chlorides. Like hydrocarbons, liquid alkyl halides are insoluble in water; they are miscible with one another and with hydrocarbons and ether. Iodides are noted for their unusually high refractive indices (the iodine atom is most strongly polarized), and fluorides, for their low refractive indices. Especially interesting are alkyl perfluorides, C_nF_{2n+2}. In spite of the immense increase of molecular weight as compared with alkanes (approximately, fourfold), their boiling points differ little from those of the corresponding hydrocarbons. This points to the very small van der Waals forces exhibited by the fluorine atom in organic fluorine derivatives, which is attributed to its low polarizability. In other words, the fluorine atom, particularly in comparison with the iodine atom, holds firmly its elec

TABLE 2.1. Physical Properties of Halogen Derivatives of Alkanes

Halogen derivative (X = halogen)	Melting point, °C				Boiling point, °C				Density d_4^{20}			
	F	Cl	Br	I	F	Cl	Br	I	F	Cl	Br	I
CH_3X	−141.8	−97.7	−93.6	−66.1	−78.6	−24.22	3.56	42.5	0.877 (d_4^{-79})	0.991 (at −25°C)	1.732 (d_0^0)	2.279
C_2H_5X	−143.2	−138.7	−119	−108.5	−37.7	+12.2	38.0	72.2	0.816 (at −37°C)	0.921 (d_4^0)	1.430	1.993
C_3H_7X	−159	−122.8	−109.8	−101.4	−3.2	47.2	70.9	102.4	0.778 (at −3.2°C)	0.890	1.353	1.747
n-C_4H_9X	−134	−123.1	−112.4	−103.5	+32.0	78	101.6	131	0.776	0.884	1.299	1.617
n-$C_5H_{11}X$ (primary)	<−80	−99	−88.0	−85.6	62.8	108.2	128.9 (at 740 mm Hg)	156	0.788	0.883	1.246 (d_4^0)	1.517
n-$C_6H_{13}X$ (primary)	−103	−83	−85	—	93.2	132.4	156	180	0.799	0.872	1.170	1.441
CH_2X_2	—	−96.7	−52.8	+5-6	−51.6	40.1	98.2	180 (dec.)	0.909	1.336	2.495	3.325
CHX_3	−163	−63.5	6-7	119	−82.2	61.3	149.5	210 (dec.)	1.52 (at −100°C)	1.498 (d_4^{15})	2.890	4.008
CX_4	−184	−22.8	−48.4 (α) −90.1 (β)	171 (dec.)	−128	76.8	189.5	90-100 (subl.)	1.96 (at −184°C)	1.595	3.42	4.32
CH_2X-CH_2X	—	−35.3	−9.97	81-82	+10; +30.7	83.7	131.6	Dec.	—	1.257	2.170 (d_4^{25})	2.132 (d_4^{10})
CH_3CHX_2	−117	−96.7	−63	—	−24.7	57.3	110	179	—	1.174	2.089	2.84 (d_4^0)

trons. This accounts for the non-wettability of articles made from polymeric perfluoroalkanes by liquids and for their poor adhesion. Owing to these properties the high-molecular-weight material polytetrafluoroethylene (Teflon), which is produced by the polymerization of tetrafluoroethylene and is a mixture of the higher members of the series C_nF_{2n+2}, has found application, for example, as a material for making bearings.

It should be noted that the interatomic distances C—X in halogen derivatives with several halogen atoms at one carbon atom are smaller than those in alkyl halides. This is especially pronounced in fluorine derivatives: the C—F distance is 1.39 Å in CH_3F, 1.332 Å in CHF_3 and 1.35 Å in CH_2F_2.

This also accounts for the higher chemical inertness of this type of polyhalogen derivatives (see page 107).

C. Chemical Properties of Halogen Derivatives

The hydrocarbon chain of alkyl halides retains the chain properties of alkanes. The most important type of reaction for alkyl halides is the substitution (replacement or displacement) reaction: the exchange of a halogen atom for other halogens or other monovalent groups of atoms under the action of water, bases and salts. An example is the exchange of a chlorine atom for iodine (the action of NaI) mentioned in the consideration of methods for synthesis of halogen derivatives:

$$C_2H_5Cl + NaI \longrightarrow C_2H_5I + NaCl$$

or the exchange of an iodine atom for a fluorine atom (the action of AgF).

Formally, these transformations resemble the ion exchange reaction:

$$KCl + NaI \longrightarrow KI + NaCl$$

A fundamental distinctive feature of such exchange reactions in organic chemistry is that they proceed at a very slow rate. The mechanism of this kind of reaction will be discussed later in the book (see pages 103 and 120).

The hydrolysis of halogen derivatives by water also proceeds very slowly at elevated temperature and results in the replacement of a halogen atom by the hydroxyl group of water and in the formation of an alcohol:

$$RX + H_2O \longrightarrow ROH + HX$$

This reaction is the reverse of the preparation of halogen derivatives from alcohols and hydrogen halides.

The exchange of a halogen for a hydroxyl group takes place at a faster rate if moist silver oxide is used:

$$2RX + Ag_2O + H_2O \longrightarrow 2ROH + 2AgX$$

When a caustic alkali is used, the exchange (reaction 1) proceeds even faster but is complicated by the side-reaction of splitting-off of hydrogen halide with the formation of an olefin (reaction 2):

$$C_nH_{2n+1}X + NaOH \begin{cases} \longrightarrow C_nH_{2n+1}OH + NaX & (1) \\ \longrightarrow C_nH_{2n} + NaX + H_2O & (2) \end{cases}$$

With a methyl halide, from which no olefin can be formed, the reaction occurs only according to scheme (1). In the case of halogen derivatives with a halogen atom at a tertiary carbon atom the reaction proceeds entirely by route (2); the same route predominates for secondary halogen derivatives. Reaction (2) belongs to the category of **elimination reactions** which are the reverse of addition reactions.

Numerous exchange reactions are known between halogen derivatives and salts of inorganic and organic acids, which proceed according to scheme (1). The following are examples of such reactions:

$$RX + NaCN \longrightarrow \underset{\text{A nitrile}}{R-C\equiv N} + NaX$$

$$RX + NaO-\overset{\overset{O}{\|}}{C}-CH_3 \longrightarrow \underset{\text{An ester}}{R-O-\overset{\overset{O}{\|}}{C}-CH_3} + NaX$$

$$RX + NaSH \longrightarrow \underset{\text{A mercaptan}}{RSH} + NaX$$

$$2RX + Na_2S \longrightarrow \underset{\text{A sulphide}}{R_2S} + 2NaX$$

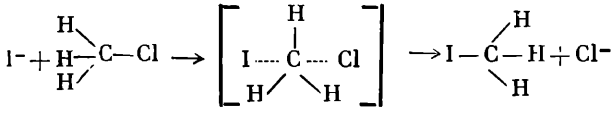
$$RX + 2NH_3 \longrightarrow \underset{\text{An amine}}{RNH_2} + NH_4X$$

These reactions render alkyl halides indispensable for organic synthesis. They serve as alkylating agents and are used for introducing alkyl groups into organic compounds.

The iodine atom undergoes an exchange reaction most readily (is the most mobile), which is ascribed to its high polarizability, but alkyl iodides are relatively expensive and can therefore be used only for synthesis in the laboratory. The chlorides and bromides differ to a lesser extent in reactivity and therefore preference is given to more available alkyl chlorides for synthesis on an industrial scale. Alkyl fluorides are not suitable for alkylations since fluorine is too inert due to its low polarizability.

The exchange of a halogen can be carried out by two different mechanisms which, as suggested by Ingold, are known as the S_N1 mechanism (**unimolecular nucleophilic substitution**) and the S_N2

mechanism **(bimolecular nucleophilic substitution).*** The bimolecular S_N2 substitution reaction is a single-stage process and involves the attack on the carbon atom by a nucleophile, the formation of a new bond due to the electrons of the nucleophile and the simultaneous rupture of the original carbon-halogen bond. For example, the reaction of methyl chloride with an iodide ion may be depicted as follows:

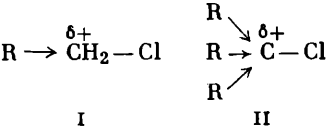


In the transition state (an intermediate complex), chloride and iodide ions are loosely bound to the carbon and so five atoms are attached to the central carbon atom. Four atoms (three hydrogens and one carbon atom) lie in the same plane and the substitution axis I—C—Cl is perpendicular to it. Thus, in the transition state the hydrogen atoms are pulled into a single plane, and at the end of the process they again occupy the positions at the axes of a tetrahedron. The net result is that the molecule has been turned inside out "like an umbrella in a strong wind". Reactions that follow the S_N2 mechanism are kinetically reactions of the second general order, i.e., their rates are expressed by equations of the type:

$$\frac{d[CH_3Cl]}{dt} = k[I^-][CH_3Cl]$$

The rate constants of reactions proceeding by the S_N2 mechanism depend on the nucleophilic nature of the reagent. For instance, the hydroxyl ion is a stronger nucleophilic reagent than water, and the hydrolysis by alkali proceeds faster.

The structure of an alkyl halide is also of great importance: primary alkyl halides (I) react more rapidly than secondary ones, and the more so than tertiary halides. This is accounted for as follows. Alkyl groups repel bonding electrons (the positive inductive effect, see page 244) thereby suppressing partly the low positive charge on the carbon atom, as a result of which the efficiency of attack on the carbon atom by a nucleophilic particle is decreased:



I II

* The letter S stands for substitution and N for nucleophilic; the numerals indicate the molecularity of the reaction.

The more seldom S_N1 mechanism involves two stages. At the first reversible stage, which is very slow, the alkyl halide undergoes ionization under the influence of a solvent, followed by the reaction of the resulting carbonium ion with the nucleophile:

$$\begin{array}{l} H_3C \\ H_3C-C-Cl \\ H_3C \end{array} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \begin{array}{l} H_3C \\ H_3C-\overset{+}{C} \\ H_3C \end{array} + Cl^-$$

$$(CH_3)_3\overset{+}{C} + X^- \xrightarrow{k_2} (CH_3)_3CX$$

It should be emphasized that the rate constant for the forward reaction at the first step, k_1, is much lower than that of the reverse reaction k_{-1}, and than k_2, and the cation is immediately consumed as formed. The reaction is termed monomolecular or unimolecular because its kinetics are determined by the first slow unimolecular step. The velocity of the reaction is expressed by the following equation:

$$\frac{d[RCl]}{dt} = k_1[RCl]\left\{1 + \frac{k_{-1}[Cl^-]}{k_2[X^-]}\right\}^{-1}$$

The concentration of chloride ions increases as the reaction progresses and is then slowed down with time. The reaction can be retarded deliberately by addition of metal chlorides. (These added compounds must not affect the occurrence of the reaction by the S_N2 mechanism.) From the equation given above it is seen that if the concentration of chloride ions is very high, the entire expression simplifies to the following:

$$\frac{d[RCl]}{dt} = k_1[RCl]$$

It must be stressed here that the S_N1 mechanism can be accomplished not in all but only in such polar solvents which contribute to the elimination and binding of the anion to be replaced (electrophilic solvents). Examples of such solvents are alcohol, water, formic acid, which are capable of forming hydrogen bonds with a halide ion. The occurrence of an alkylation reaction by this mechanism is encouraged by silver salts, say, AgCN, since silver ions expel the halide ion and bind it firmly.

An evidence that the reactions of *tert*-butyl chloride in a water-acetone solution occurs by the S_N1 mechanism is the following. This alkyl halide is hydrolysed by an excess of water at a definite rate. When equimolar amounts of sodium azide are introduced, *tert*-butyl alcohol is no longer formed, the only product being *tert*-butyl azide:

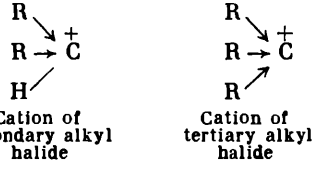
$$(CH_3)_3CCl \rightleftarrows (CH_3)_3C^+Cl^- \begin{cases} \xrightarrow{H_2O} (CH_3)_3COH \\ \xrightarrow[NaN_3]{} (CH_3)_3CN_3 \end{cases}$$

The rate constant for the reaction of the alkyl chloride, however, remains the same as before (the velocity of a reaction is the rate of decrease of the concentration of *tert*-butyl chloride in solution). This is explained by the fact that sodium azide and water react not with a molecule of alkyl chloride but with the transiently and slowly formed cation. It means that the competition between the nucleophiles takes place at the second step of the reaction when the overall rate has already been established by the first rate-determining step.

A direct (spectral) evidence for the existence of alkyl carbonium ions was provided by G. A. Olah in 1963. Dissolving tertiary and secondary alkyl fluorides in a strong electrophilic solvent, antimony pentafluoride, he obtained solutions of carbonium salts stable at a temperature of —80 to —100°C (see Volume IV).

$$(CH_3)_2CHF + SbF_5 \rightleftarrows [(CH_3)_2CH]^+[SbF_6]^-$$

Tertiary alkyl halides react by the S_N1 mechanism more readily than secondary ones. This is attributed to the greater energy favourableness of tertiary alkyl cations since the positive charge on these cations is suppressed by a larger number of alkyl groups due to the positive inductive effect of the latter (see page 244):



Primary alkyl halides do not react by this mechanism under ordinary conditions. As pointed out earlier, they react by the S_N2 mechanism.

It should however be noted that not all primary halogen derivatives react rapidly. Exceedingly interesting is the recently discovered inertness of the halogen derivatives of hydrocarbons having a neostructure, say, $(CH_3)_3CCH_2Cl$, in exchange reactions. Their inertness is explained by the fact that in the transition state it is difficult for the bulky $(CH_3)_3C$ group to arrange itself at a carbon atom simultaneously with the entering and leaving substituents and two hydrogens (*steric hindrances*).

An especially important reaction of alkyl halides is the reaction leading to the formation of organomagnesium compounds (Grignard reagents) by the action of an ethereal solution of an alkyl halide (iodide, chloride or bromide, but not fluoride) on shavings of metallic magnesium:

$$RX + Mg \longrightarrow RMgX$$

The reaction with lithium proceeds in a similar way:

$$RX + 2Li \longrightarrow RLi + LiX$$

These organometallic compounds find the various applications in organic synthesis.

Polyhalogen compounds react in a different way, except dihaloalkanes with a sufficiently long carbon chain (consisting of at least four carbon atoms) between the halogen atoms. Other reactions involving polyhaloalkanes (polyhalogenoalkanes) and halogens attached to different carbon atoms are analogous to the reactions of alkyl halides. An example is the reaction of 1,2-dichloroethane:

$$ClCH_2-CH_2Cl + Ag_2O + H_2O \longrightarrow HOCH_2-CH_2OH + 2AgCl$$
$$ClCH_2-CH_2Cl + 2KCN \longrightarrow N\equiv C-CH_2-CH_2-C\equiv N + 2KCl$$

The halogen derivatives of alkanes with two or more halogen atoms at a single carbon atom are considerably more inert and, as a rule, they are hydrolysed under more drastic conditions:

$$R-CCl_2-R' + H_2O \xrightarrow{K_2CO_3} R-\overset{\overset{O}{\|}}{C}-R' + 2HCl$$

$$R-CCl_3 + 2H_2O \xrightarrow{H_2SO_4} R-\overset{\overset{O}{\|}}{C}-OH + 3HCl$$

$$R-CCl_3 + 4NaOH \longrightarrow R-\overset{\overset{O}{\|}}{C}-ONa + 3NaCl + 2H_2O$$

The hydrolysis of chloroform by alkali yields sodium formate:

$$HCCl_3 + 4NaOH \longrightarrow H-\overset{\overset{O}{\|}}{C}-ONa + 3NaCl + 2H_2O$$

It is possible, however, that the mechanism of conversion of chloroform into the formate is more complicated than in the above reaction equation. The point is that the action of strongly alkaline agents, say, alkali-metal alkoxides, on chloroform (and fluoroform) leads to the elimination of a hydrogen halide and to the formation of derivatives of divalent carbon—dihalocarbenes (dichlorocarbene and difluorocarbene, CCl_2 and CF_2). These unstable substances are often cited as intermediate products in haloform reactions taking place in alkaline solution. Possibly, in this reaction too, there is formed dichlorocarbene as an intermediate, which then reacts with alkali and loses the two remaining chlorine atoms due to hydrolysis.

In 1964, Köbrich described the reaction of methylene chloride and chloroform with butyl-lithium at —112°C, leading to the formation of lithium derivatives of these halides:

$$CH_2Cl_2 + C_4H_9Li \longrightarrow LiCHCl_2 + C_4H_{10}$$
$$CHCl_3 + C_4H_9Li \longrightarrow LiCCl_3 + C_4H_{10}$$

The organometallic compounds obtained are somewhat stable up to —60°C and can be used at that temperature for syntheses. The lithium derivative of methylene chloride is more stable than that of chloroform. When these compounds decompose, the corresponding halocarbenes are formed.

The reactions of methylene chloride and chloroform with butyllithium show the increased (as compared with hydrocarbons) tendency of the hydrogen of halogen derivatives towards ionization. We shall encounter this phenomenon later in the book (see pages 128 and 190).

Perfluoroalkanes of the general formula C_nF_{2n+2} are distinguished for their exceptional chemical inertness; they do not enter into exchange reactions with the most aggressive reagents even under severe conditions. Polytetrafluoroethylene (Teflon) is a chemically more stable material than platinum; it does not change when heated to a high temperature with a strong acid, alkali or oxidizing agent.

D. Structure Determination

The skeleton structure of a halogen derivative can be determined by deriving the parent hydrocarbon from it. The reduction of halogen derivatives to a hydrocarbon is accomplished by the action of magnesium in ether with subsequent hydrolysis of the organomagnesium compound or (in the case of polyhalogen derivatives) by the action of hydrogen iodide on heating in a sealed tube. If a halogen derivative had two halogen atoms arranged at adjacent carbon atoms, magnesium splits off the two halogen atoms and both carbons become linked to each other by a double bond. The site of this double bond is established through the oxidation of the unsaturated compound formed, followed by the rupture of the chain at the double bond (such reactions will be discussed in Sec. 3.1). In other cases, a halogen derivative is subjected to hydrolysis: a monohalogen derivative changes into an alcohol, a dihalogen derivative into a dihydric alcohol (a glycol) or into an aldehyde or ketone if both halides reside at one carbon atom. All these compounds can be easily identified by their reactions. The disposition of the hydroxyl group (OH) in these compounds or of the carbonyl group (CO) is established through oxidation to acids (these reactions will be considered in sections dealing with alcohols, aldehydes, and ketones).

I. The Chemical Reaction

We have already discussed many reactions of organic compounds—exchange, elimination and addition reactions. Equations that described these reactions were largely nothing more than the stoichiometric result which may correspond to different reaction mechanisms, different intermediate products and to different rates. Though a stoichiometric equation provides only a minimum knowledge of the nature of a particular reaction, this minimum is absolutely necessary. Using a stoichiometric equation, one can calculate the required amount of reagents, the yield of reaction products and the heat of reaction which is independent of the conversion route but is only a function of the initial and final states.

The theory of chemical reactions consists of two large sections—the theory of chemical equilibria and the theory of the rate of chemical reactions (kinetics). Both these theories constitute the subject matter of physical chemistry. Certain inferences following from these theories are however needed in the study of organic chemistry so that the nature of organic reactions is more deeply understood.

(A) Chemical Equilibrium

In organic chemistry, many pairs of reagents can react not in one but in several parallel, competing directions. For example,

$$CH_3CH_2Cl + KOH \begin{cases} \rightarrow CH_2=CH_2+KCl+H_2O \\ \rightarrow CH_3CH_2OH+KCl \end{cases}$$

Under certain conditions (in solutions or in the gaseous phase) other substances react only in a single direction. The reactions involved may proceed in this sole direction to completion (irreversible reactions) or in the forward and reverse directions (reversible reactions).

In writing equations for reversible reactions the equality sign is replaced by a double arrow, the arrows being pointed in opposite directions:

$$CH_3OH + HCl \rightleftarrows CH_3Cl + H_2O$$

In the case of reversible reactions, a dynamic equilibrium sets in, i.e., the reaction is complete when the reactants and products are present in the system in definite concentrations. The ratio of the concentrations is governed by the law of mass action, according to which at a given temperature the ratio of the product of the concentrations of the final reaction products to the product of the concentrations of the reactants (each concentration being raised to the

power equal to the number of moles of a given substance involved in the reaction) is a constant quantity:

$$aA + bB \rightleftarrows dD + eE$$

$$K_c = \frac{c_D^d \cdot c_E^e}{c_A^a \cdot c_B^b} \tag{1}$$

where K_c is the equilibrium constant which is a function of temperature; at constant temperature in dilute solutions it is independent of the initial concentrations.*

For more concentrated solutions, the concentrations c must be replaced by the activities a in the equation for the equilibrium constant:

$$K_a = \frac{a_1^d \cdot a_2^e \ldots}{a_1^a \cdot a_2^b \ldots} \tag{2}$$

The activity is given by

$$a = c\gamma$$

where c is the concentration in moles per 1000 g of solvent (or in other units) and γ is the activity coefficient. The value of activity coefficient is found experimentally. Special tables are available in the literature, from which the required value of activity coefficient can be found. For dilute solution $\gamma \to 1$, and use may therefore be made of the quantity K_c.

Activity coefficients vary, depending on the concentration and temperature, in different ways for different substances and serve, as it were, as a correction for the concentration, allowing one to apply the law of mass action to solutions of any concentration. That is why K_a is preferred to K_c. The equilibrium constant K_a is called the **thermodynamic equilibrium constant.**

Thermodynamics shows that there exists a relationship between the equilibrium constant and a number of thermodynamic functions. Thus, for example, the relation between the decrease in the isochoric-isothermal potential, ΔF, the maximum reaction work at constant volume A_V and the equilibrium constant K_c is expressed by the equation:

$$A_V = -\Delta F = RT \ln K_c - RT \ln \frac{c_{D,0}^d \cdot c_{E,0}^e \cdots}{c_{A,0}^a \cdot c_{B,0}^b \cdots} \tag{3}$$

where F is the isochoric-isothermal potential (the Helmholtz free energy**); $c_{A,0}^a$, $c_{B,0}^b$, etc., are the non-equilibrium concentrations of the reactants and products.

* The yield of the desired product, however, depends on the concentration of substances in the original mixture.

** This quantity is sometimes called the free energy at constant volume.

If the initial conditions are chosen to be equal to unity, the maximum work at constant volume will be equal to $-\Delta F$ when the reactants with concentrations $c_i = 1$ are being transformed into the final reaction products with concentrations $c_i = 1$:

$$A_V^0 = RT \ln K_c = -\Delta F^\circ \tag{4}$$

that is, will be equal to a decrease in the Helmholtz free energy.

The Helmholtz free energy F of a system is known to mean that part of the energy of the system which can be transformed into work in an isothermal reversible process:

$$F = U - TS \tag{5}$$

where U = internal energy
T = absolute temperature
S = entropy of the system.

The equilibrium constant may be expressed not through the concentrations but in terms of the partial pressures of the reactants and products:

$$K_P = \frac{P_D^{\mathrm{d}} \cdot P_E^{\mathrm{e}} \cdots}{P_A^{\mathrm{a}} \cdot P_B^{\mathrm{b}} \cdots} \tag{6}$$

In this particular case, there also exists a relation between the equilibrium constant K_P and the thermodynamic functions. The decrease in G in constant-pressure and constant-temperature processes is equal to the maximum useful work at constant pressure A_P, i.e., the maximum work minus the work of expansion:

$$A_P = -\Delta G = RT \ln K_P - RT \ln \frac{P_{D,0}^{\mathrm{d}} \cdot P_{E,0}^{\mathrm{e}} \cdots}{P_{A,0}^{\mathrm{a}} \cdot P_{B,0}^{\mathrm{b}} \cdots} \tag{7}$$

where G is the Gibbs free energy (free energy at constant pressure); $P_{A,0}^a$, $P_{B,0}^b$, etc., are the non-equilibrium partial pressures of the reactants and products.

The function G is defined by the equation

$$G = F + PV = U - TS + PV = H - TS \tag{8}$$

where $H = U + PV$ = function of the state of the system known as the enthalpy
U = internal energy
P = pressure
V = volume.

The equilibrium constants K_c and K_P for one and the same reaction between ideal gases are interrelated by the following equation:

$$K_P = K_c (RT)^{\mathrm{a'+b'+c'-a-b-c}\ldots} \tag{9}$$

Obviously, for reactions taking place without any change of the number of molecules ($a + b + c \ldots = a' + b' + c'$), the constants K_P and K_c are equal to each other.

If the partial pressure of each of the components in the original mixture is equal to unity, Eq. (7) assumes the following form:

$$-\Delta G = RT \ln K_P \tag{10}$$

For a process at constant temperature we obtain from Eq. (8):

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{11}$$

Proceeding from Eqs. (8) and (10) and passing over to common logarithms, we find:

$$-2.303\, RT \log K_P = \Delta H - T\Delta S \tag{12}$$

$$(R = 1.986 \text{ cal/deg C})$$

The quantities ΔH and ΔS can be determined from experimental data; $-\Delta H$ at constant pressure is equal to Q_P, which is the heat of reaction at constant pressure, determined calorimetrically or calculated according to Hess's law from the heats of other reactions; ΔS is the algebraic sum of the entropy values for the participants in the reaction, equal to

$$\Delta S = a'S_1' + b'S_2' + c'S_3' + \ldots - aS_1 - bS_2 - cS_3 - \ldots \tag{13}$$

The entropy of each reactant is determined by integration of C_P/T from the absolute zero with account taken of the heats of phase transitions:

$$S = \int_0^T \frac{C_P}{T}\, dT + \sum \frac{L_\Phi}{T_\Phi} \tag{14}$$

where C_P = heat capacity at constant pressure
L_Φ = heat of a polymorphic transformation, sublimation, melting, evaporation
T_Φ = respective absolute temperature.

The way in which ΔG (and hence the equilibrium constants) is calculated from Eqs. (11) through (14) is known as an estimation according to the third law of thermodynamics, from which Eq. (14) follows. Another way for calculating ΔG (the statistical method) is applicable only to reactions between gases. In this method, the entropy of each participating gaseous substance is calculated by the methods of statistical thermodynamics on the basis of the molecular parameters of the substance, i.e., the vibration frequencies, moment of inertia and excitation potentials of the molecule, which in their turn can be found from spectroscopic, electronographic and other data for the molecule of each reactant.

At present there are special tables containing the heats of formation of substances from their constituent elements and entropies under standard conditions (25°C and 1 kg/cm²). Using tabulated data, one can easily calculate the heat of reaction, $Q_P = -\Delta H$ and ΔS from Eq. (13) and then ΔG from Eq. (11). To recalculate ΔG for a different temperature, one has to know the heat capacities (see below). Having calculated ΔG at a specified temperature, one can find K_P from Eq. (10) or calculate ΔF and K_c using Eqs. (8) and (4), respectively.

Only a small number of relatively simple organic compounds have been studied and only for them can one find the required information in tabular form.

The temperature dependence of the equilibrium constant is defined by the following equations:

$$\left(\frac{\partial \ln K_c}{\partial T}\right)_V = \frac{\Delta U}{RT^2} \tag{15}$$

$$\left(\frac{\partial \ln K_P}{\partial T}\right)_P = \frac{\Delta H}{RT^2} \tag{16}$$

where ΔU = increment in internal energy, equal to the heat of reaction at constant volume

ΔH = increment in enthalpy, equal to the heat of reaction at constant pressure.

Integration (with simplifying assumption that the heat effect of the reaction is independent of temperature) leads to Eq. (17) for a constant-volume process:

$$\ln K_{c'_2} = \ln K_{c'_1} + \frac{\Delta U\,(T_2 - T_1)}{RT_1T_2} \tag{17}$$

and to Eq. (18) for a constant-pressure process:

$$\ln K_{P'_2} = \ln K_{P'_1} + \frac{\Delta H\,(T_2 - T_1)}{RT_1T_2} \tag{18}$$

Passing over to common logarithms and introducing the numerical value of the gas constant R, we obtain:

(a) at constant volume

$$\log K_{c'_2} = \log K_{c'_1} + \frac{\Delta U\,(T_2 - T_1)}{4.576T_1T_2} \tag{17a}$$

(b) at constant pressure

$$\log K_{P'_2} = \log K_{P'_1} + \frac{\Delta H\,(T_2 - T_1)}{4.576T_1T_2} \tag{18a}$$

In actual practice, however, the heat of reaction is usually dependent on temperature and this relationship is defined by Kirchhoff's law:

$$\Delta U_T = \Delta U_{T_0} + \int_{T_0}^{T_1} \sum_{1}^{K} \nu_i C_{Vi}\, dT \tag{19}$$

$$\Delta H_T = \Delta H_{T_0} + \int_{T_0}^{T_1} \sum_{1}^{K} \nu_i C_{Pi}\, dT \tag{20}$$

where C_V and C_P are the molar heat capacities of the reactants at constant volume and at constant pressure, respectively; ν is the corresponding number of moles.

The heat capacities in their turn depend on temperature; this relationship is expressed by a power series. On integration the power dependence indicated has to be placed after the integral sign.

Let us turn to Eq. (12) again:

$$\log K_P = -\frac{\Delta H - T\Delta S}{2.303RT} = \frac{T\Delta S - \Delta H}{2.303RT} = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} \tag{12a}$$

The logarithm of the equilibrium constant of a reaction at a given temperature is a function of the difference written on the right-hand side of the series of equations. Recall that $-\Delta H$ is used to denote the heat evolved in the reaction. The logarithm of the constant (and the more so the constant itself) will hence be the higher the more exothermic is the reaction, other conditions being equal. A second term, which is of no less importance, is one containing an increment of the entropy ΔS, which can provide high values of the equilibrium constant for the case of endothermic reactions too.

What reaction factors does the increment of entropy depend on? It depends on the change from more orderly systems to more random (disorganized) ones. For example, the cyclization (e.g., of acetylene to benzene) is a process with a decrease of entropy. In cracking, the entropy increases. On hydrogenation of solid charcoal by hydrogen with the formation of a mixture of alkanes the disturbance of the orderliness of the crystal (for example, graphite) with a change to less ordered chains of alkanes (with a larger number of degrees of freedom) introduces a positive term into the entropy expression, while the transformation of gaseous hydrogen to the combined state gives a negative term.

It should however be remembered that the overwhelming majority of organic reactions proceed not unambiguously, according to a single reaction equation; almost all organic reactions are complicated and are thought to consist of a series of consecutive and parallel elementary reactions occurring at different rates. Some of these concurrent reactions are reversible and proceed until equilibri-

um is reached; others go to near completion. For a very large number of cases, it is not possible to split a complicated overall reaction into simpler ones, locate the position of equilibrium and find the equilibrium constant (or the quantity ΔG) for each elementary reaction separately. If this proves to be possible, then, with the equilibrium being set up, we can calculate the complex composition of the reaction mixture. Not infrequently, this task is so formidable that it can be resolved only with the aid of modern computing technique.

(B) Reaction Rate

In many cases, it is pointless to try to take into account the equilibria of all the elementary reactions or steps that make up the ordinary overall complex reaction in organic chemistry. The point is that competing reactions run at greatly differing rates so that in any limited interval of time some of the reactions proceed to completion, while others remain at the initial stage.

It is the relative rates of the individual elementary reactions or steps that determine in what direction for a given period of time the major amount of the reactants will have reacted. Competition between the reaction rates also governs the yield of the products for a specified time interval.

The rate of a reaction, or alternately, the speed or velocity of a reaction, can be expressed as the derivative of the amount of the substance that has reacted in time t (i.e., in terms of the time rate of disappearance of the reactant; hence the negative sign):

$$v = -\frac{dc}{dt} \tag{21}$$

A measure of the amount of substance is its concentration c.

In kinetics, the concepts of the **molecularity** and **order of a reaction** are distinguished.

The molecularity of a reaction reflects the mechanism of an elementary act and refers to the number of molecules or particles involved in a collisional process. For instance, unimolecular reactions are reactions involving the conversion of one molecule; bimolecular reactions are those involving the conversions resulting from the collision of two molecules, and so on. The stoichiometric equation of a reaction corresponds to the molecularity only in the case of simple reactions (reactions in which the end product is obtained immediately, directly from the starting material, without any intermediate steps). In this case, the rate of a unimolecular reaction, i.e., the rate of disappearance of the reactant is proportional to its concentration:

$$v = -\frac{dc}{dt} = kc \tag{22}$$

where k is the proportionality coefficient.

The rate of a bimolecular reaction is given by the following equation:

$$v = -\frac{dc}{dt} = kc'c'' \tag{23}$$

or, in the case of conversion of one species,

$$v = -\frac{dc}{dt} = kc^2 \tag{24}$$

that is, the rate of a reaction is proportional to the square of the concentration (or to the product of the concentrations).

From the equations given above it can be seen that in one case, in the rate expression (22), the concentration is raised to the first power, and in Eq. (24) it is raised to the second power. The sum of the exponents of the concentration terms in the rate expression is known as the **reaction order** (first order, second order, etc.). It is obvious that only in the case of simple reactions will the molecularity of the reaction coincide with reaction order. In view of this, Eq. (22) is the equation for the rate of a first-order reaction, while Eqs. (23) and (24) are equations for the rates of second-order reactions.

Integration of Eq. (22) between the limits c_1 at time t_1 and c_2 at time t_2 yields an expression for the first-order rate constant:

$$k' = \frac{1}{t_2 - t_1} \ln \frac{c_1}{c_2} \tag{22a}$$

This is the rate law* for a first-order reaction; the dimensions for the first-order rate constant are a second raised to the power -1 (sec^{-1}).

The integral form of Eq. (23) if $c' = c''$ (for the time period from t_1 to t_2) is as follows:

$$k'' = \frac{1}{t_2 - t_1} \left(\frac{1}{c_1'} - \frac{1}{c_2''} \right) \tag{23a}$$

This is the rate law for second-order reactions; the second-order rate constant is expressed in (litres/moles per sec).

In a general case ($c' \neq c''$) the integration of Eq. (23) will lead to the following equation

$$k'' (t_2 - t_1) = \frac{1}{c_1'' - c_1'} \ln \frac{c_1' \cdot c_2''}{c_1'' \cdot c_2'} \tag{23b}$$

---

* The expression which gives the reaction rate as a function of the concentration of each of the substances affecting the rate is called the **rate law** for the reaction.— *Tr.*

As examples of unimolecular reactions may be cited the numerous reactions of isomerization, tautomerization (interconversion of two tautomers), dissociation into ions (i.e., electrolytic dissociation) and homolytic cleavage.

Bimolecular reactions constitute the most common type of reactions. As examples may be cited exchange reactions in the series of primary halogen derivatives under the action of OH^-, CN^-, RCO^-,

etc.

Third-order reactions are encountered less frequently since the probability of a simultaneous collision of three molecules is considerably lower. Their rate is evidently proportional to the product of the concentrations of the three substances:

$$-\frac{dc}{dt} = k'''c'c''c''' \tag{25}$$

In the case of equimolecular initial concentrations the term $k'''c'c''c'''$ changes to $k'''c^3$or, in the integral form,

$$k''' = \frac{1}{t_2 - t_1} \cdot \frac{1}{2c_1^2}\left[\left(\frac{c_1}{c_2}\right)^2 - 1\right] \tag{26}$$

Equation (22a) for the rate constant of a first-order reaction may now be rewritten in the following form:

$$kt_2 - kt_1 = \ln c_1 - \ln c_2 \tag{27}$$

Considering that the initial time t and the initial concentration c_1 (the concentration at the initial moment) are constant, and that only t_2 and c_2 are variables, we plot t_2 along the abscissa and $\ln c_2$ along the ordinate. We thus obtain a straight line from which it is possible to determine the value of rate constant for the reaction. To this end, it is more convenient to pass from natural to common logarithms:

$$-\log c_2 = 0.4343kt_2 - 0.4343kt_1 - \log c_1 \tag{28}$$

Since in this equation t_2 is an independent variable, $-\log c_2$ is a function, and the remaining terms are constant, we arrive at the conclusion that the coefficient $0.4343k$ for t_2 is the slope of the straight line to the abscissa, from which the value of k can be found.

Reasoning in a similar way as regards the equation for a second-order reaction [Eqs. (23) and (24)], we may conclude that a straight line is obtained by plotting the time along the abscissa and $\log (c_2''/c_2')$ along the ordinate if the constant k remains constant.

Indeed, in Eq. (23b) the time t_2 is an independent variable and $\ln (c_2''/c_2')$ is a function. Equation (23b) can be rewritten thus:

$$\ln \frac{c_2''}{c_2'} = k''(c_1'' - c_1')t_2 + \ln \frac{c_1'}{c_1''} + k''t_1 \tag{29}$$

and, after changing from natural to common logarithms, we have:

$$\log\frac{c_2''}{c_2'} = 0.4343k''(c_1'' - c_1')t_2 + \log\frac{c_1'}{c_1''} + 0.4343k''t_1 \qquad (30)$$

The third and fourth terms in the above equations are constant. The slope of the curve [with t_2 plotted along the abscissa and $\log(c_2''/c_2')$ along the ordinate] is equal to $k''(c_1'' - c_1')\,0.4343$, from which it is easy to find the value of k'':

$$k'' = \frac{\tan\alpha}{(c_1'' - c_1')\,0.4343} \qquad (31)$$

With a large excess of one of the reactants the bimolecular reaction will basically proceed according to the first-order equation (*pseudounimolecular reaction*) since it will not be dependent on the change (vanishingly small) of the concentration of the excess reagent. Typical examples of such pseudounimolecular reactions are hydrolysis reactions in aqueous solution (a large excess of water). Any bimolecular reaction can in fact be conducted as a pseudounimolecular reaction by introducing a large excess of one of the reactants.

If the reaction passes through a succession of stages (i.e., is a multistep reaction), the overall rate is determined by the rate of the slowest step of the reaction and kinetic measurements allow one to judge only about that step. An example is the hydrolysis of tertiary alkyl halides which are converted by the action of water into alcohols (in a solvent) in two steps:

$$(CH_3)_3CCl \longrightarrow (CH_3)_3C^+ + Cl^-$$
$$(CH_3)_3C^+ + H_2O \longrightarrow (CH_3)_3COH + H^+$$

The first step, the ionization of the tertiary alkyl halide, proceeds at a slow rate. This is evidently a unimolecular process*, and it is the rate of this slow process that is measured in the kinetic measurements of the decrease of the concentration of $(CH_3)_3CCl$ with time or of the increase in the hydrogen ion concentration with time. The second step, i.e., the bimolecular reaction of the cation $(CH_3)_3C^+$ with a molecule of water, takes place rapidly and therefore it is left out in kinetic measurements. The overall reaction proceeds according to the rate law of a first-order reaction.

The dependence of the rates of complicated reactions, whose individual steps proceed at comparable velocities, cannot ordinarily be expressed by a simple kinetic equation. The orders of such reactions are often fractional and may even vary in the course of the reaction.

For reversible reactions, when equilibrium sets in, the rate of the forward reaction is equal to that of the reverse reaction (otherwise

* More precisely, this is a pseudounimolecular process since the solvent (present in a very large excess) that makes the ions solvated is an active participant in the ionization reaction.

no equilibrium would be reached and the reaction would take place in the direction of the faster reaction rate). It is for this reason that the equilibrium constant must be equal to the ratio of the rate constants of the forward and reverse reactions:

$$K_c = \frac{k \text{ of forward reaction}}{k \text{ of reverse reaction}} \tag{32}$$

The relation between the rate constant of the reaction and temperature is expressed by the Arrhenius equation:

$$k = Ae^{-\frac{E}{RT}} \quad \text{or} \quad k = Pze^{-\frac{E}{RT}} \tag{33}$$

where k = rate constant
Pz = pre-exponential factor; it may be regarded as the experimentally determined value of A which is constant for a particular reaction and for a given set of reaction conditions
e = base of natural logarithms
R = gas constant
T = absolute temperature
E = activation energy, i.e., the amount of energy by which the energy of effectively colliding (reacting) molecules must exceed the average energy of the molecules under given conditions.

The pre-exponential factor (or the Arrhenius factor) Pz consists of two factors: z, the number of collisions of reacting molecules per second, which is calculated on the basis of the kinetic theory, and P which is the spatial factor ($P < 1$). This factor introduces a correction for the fact that only those collisions are effective (i.e., result in a chemical change), which involve molecules having a certain favourable mutual arrangement.

The Arrhenius equation shows that at a given temperature not all collisions produce a reaction and only those molecules which acquire sufficient activation energy can react to give products; their activation energy must exceed by the amount E the average energy of the molecules under specified conditions. But even in this case, not all the pairs of molecules that satisfy this requirement will enter into reaction (the fractional factor P) but only those which will collide in the most fitting geometrical way. The more complex the structure of the reactant molecules, the smaller is the fractional quantity P; for the simplest molecules the value of P is close to unity.

The energy relations between reactants and products are illustrated by the scheme shown in Fig. 2.3.

The **activation energy** may be determined experimentally by measuring the rate of a reaction at several temperatures and by plotting the calculated values of the rate constant logarithm along the ordi-

nate and the values of $1/T$ along the abscissa. Since from Eq. (33) it follows that

$$\ln k = \ln Pz - \frac{E}{R} \cdot \frac{1}{T} \tag{34}$$

the slope of the straight line obtained will then be equal to E/R.

Relation Between the Reaction Rate Constant and the Energy Parameters of the Transition State. In a chemical reaction, the system of

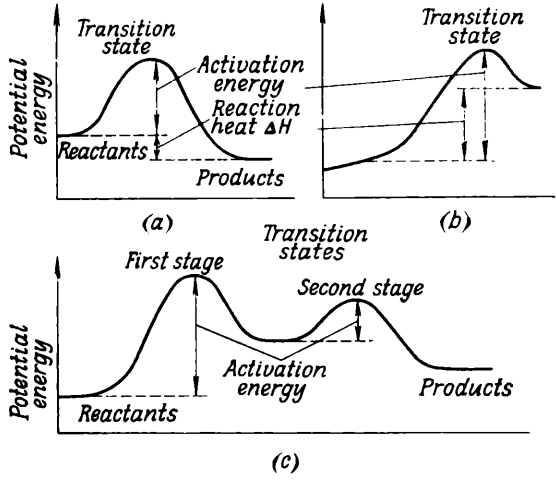
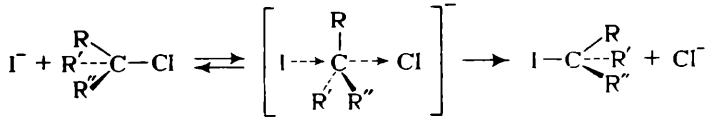


Fig. 2.3.

Energy relations between reactants and products:
(a) exothermic reaction; (b) endothermic reaction; (c) two-stage reaction with a stable intermediate product and two transition states.

reacting molecules, no matter whether it consists of a single molecule (unimolecular reaction), or two molecules (bimolecular), or of three molecules (termolecular), must be converted into the transition state (the activated complex) due to the activation energy. If the transition state is viewed from the energy considerations, then it may be characterized as the highest-energy point on the pathway from reactants to products, through which the reactant molecules must pass for the reaction to be accomplished.

Let us illustrate this by the example of the simplest bimolecular reaction, say, the exchange of chlorine for iodine in the reaction of sodium iodide with an alkyl chloride (Finkelstein reaction):



In the transition state carbon is, as it were, pentavalent, but its linkage with the two halogens is not a real stable bond, like the one in an alkyl halide. The distance between the carbon and either of the halogens is 20-40 per cent greater than that in the reactant and product, and the energy of each bond is lower. The substituent halide ion attacks the molecule from the side opposite to the halogen present in it, and in the transition state the RR′R″C grouping becomes flattened.* It is the attainment of this unstable and energy-rich transition state that the activation energy is used up for.

There are two paths from the transition state—either the return to the original reactants or the transformation into the final products. The transition state may be treated as an unstable compound and the reaction leading to its formation as a reversible chemical reaction (the rate constant k).

In the transition-state theory developed by London and Eyring, for the reaction

$$\text{Reactants} \rightleftarrows \text{Transition state}$$

there has been derived the following relation between the rate constant k and the equilibrium constant $K^{\star}$:

$$k = -\frac{\varkappa T}{h} K^{\star} \tag{35}$$

where $\varkappa$ is the Boltzmann constant equal to the gas constant R divided by the Avogadro number N_0; h is Planck's constant.

Thus, $\varkappa/h$ is a constant quantity. For any reaction at a constant temperature (300°K)

$$\frac{\varkappa}{h} T = 6 \cdot 10^{12}$$

The equilibrium constant $K^{\star}$ is related to the thermodynamic potentials in just the same way as the equilibrium constant of an ordinary reaction [see Eqs. (10) through (12)], namely,

$$\log K^{\star} = -\frac{\Delta H^{\star} - T\Delta S^{\star}}{2.303RT} \tag{36}$$

whence

$$K^{\star} = e^{-\frac{\Delta G^{\star}}{RT}} \tag{37}$$

Substituting the value of $K^{\star}$ into Eq. (35), we obtain the following expression:

$$k = \frac{\varkappa T}{h} e^{-\frac{\Delta G^{\star}}{RT}} \tag{38}$$

Hence, the rate constant of a reaction is a function of the work $\Delta G^{\star}$ which must be spent for the molecules of the reactants to

* In the final product, this grouping is found to be a mirror image of that in the starting material; see page 104.

reach the transition state. Knowing the value of $-\Delta G^{\star}$, one can calculate the reaction rate.

In an analogous way we can express $K^{\star}$ in terms of enthalpy and entropy by substituting the corresponding values into Eq. (35):

$$k = \frac{\varkappa T}{h} e^{\frac{\Delta S^{\star}}{R}} e^{-\frac{\Delta H^{\star}}{RT}} \tag{39}$$

For temperatures at which organic reactions are generally carried out, $\Delta H^{\star}$ differs but little from the activation energy E which usually reaches several or many tens of kilocalories, while the value of RT is less than 1 kcal/mole. Thus, we may assume that

$$\frac{\varkappa T}{h} e^{\frac{\Delta S^{\star}}{R}}$$

is equal to the pre-exponential factor A (or Pz) in the Arrhenius equation. Hence, the pre-exponential term is an expression of the probability of the reactant being converted into the activated complex (the entropy being proportional to the logarithm of thermodynamic probability).

2.3. Saturated Alcohols

A. Monohydric Alcohols (Alkanols)

We have already mentioned (see Introduction, Sec. 1.1, page 23), using ethyl alcohol as an example, that alcohols are the hydroxyl derivatives of hydrocarbons. A study of the halogen derivatives of saturated hydrocarbons has led to the establishment of some other relations among alkanes, alkyl halides and alcohols:

$$C_nH_{2n+2} \underset{HI}{\overset{Cl_2}{\rightleftharpoons}} C_nH_{2n+1}Cl \underset{HCl}{\overset{Ag_2O+H_2O}{\rightleftharpoons}} C_nH_{2n+1}OH$$

These interconversions can be understood only on the assumption that alcohols are the hydroxyl derivatives of alkanes—hydroxyalkanes or alkanols.

Obviously, for methane and ethane, in each of which all the hydrogen atoms are equivalent, it is possible to obtain one alcohol for each by substitution of a hydroxyl group for one hydrogen: methyl elcohol (methanol), CH_3OH, and ethyl alcohol (ethanol), CH_3CH_2OH. For propane we have two possibilities—substitution of a hydroxyl group either for one of the hydrogens of the extreme methyl groups or for one of the two hydrogens of the central methylene group. Indeed, there exist two propyl alcohols: primary propyl alcohol, in which the hydroxyl group is linked to a primary carbon atom, and secon-

dary propyl alcohol with the hydroxyl group being attached to a secondary carbon atom:

$$\underset{\text{Primary propyl alcohol}}{CH_3-CH_2-CH_2OH} \qquad \underset{\text{Secondary propyl alcohol}}{CH_3-\overset{\overset{OH}{|}}{CH}-CH_3}$$

Unfortunately, the name isopropyl alcohol is usually preferred to the correct name of *sec*-propyl alcohol.

Thus, the isomerism of alcohols, like that of substituted hydrocarbons in general, has a dual character. We may have structural isomerism, which is already familiar to us with respect to alkanes, or the isomerism occasioned by the different position of the hydroxyl group in the molecule. Beginning with the four h member of the alkane series (butane), alcohols can be derived from two different skeletons: from *n*-butane and isobutane.

Alcohols in which the hydroxyl group is attached to a primary carbon (the $-CH_2OH$ group) are called primary; those in which the hydroxyl is linked to a secondary carbon atom (the $\diagdown\!\!\diagup CHOH$ group) are termed secondary; and those with the hydroxyl being attached to a tertiary carbon atom (the $\diagdown\!\!\diagup\!\!\!\!-COH$ group) are known as tertiary alcohols.

Alkanols—the members of the homologous series of methyl alcohol (methanol)—have the general formula $C_nH_{2n+1}OH$. According to the carbinol system of nomenclature, the first member of the series, methanol, is called carbinol. The names of its homologues include the word carbinol preceded by the name of an alkyl (or other) radical that has replaced the skeletal hydrogen atom in methyl alcohol. According to the International Geneva nomenclature, the name of an alcohol is built up by replacing the final *-e* in the Geneva name of an alkane by *-ol*. The numbering of the carbon skeleton remains the same as in the parent hydrocarbon. The name is preceded by a numeral designating the hydroxyl-bearing carbon atom. If the compound is a dihydric alcohol (or a glycol), i.e., if it has two hydroxyl groups, the name will assume the ending *-diol*; and if it has three hydroxyl groups, the ending *-triol* is added to the name. For example, ethylene glycol, $HOCH_2-CH_2OH$, is called 1,2-ethanediol; glycerine (glycerol), $HOCH_2-CH(OH)-CH_2OH$, is called 1,2,3-propanetriol.

(a) *Physical Properties of Alcohols*

The physical properties of alkanols, their formulas and names—trivial and those formed according to the carbinol system and the Geneva nomenclature—are listed in Table 2.7.

TABLE 2.7. **Alkanols**

Formula	Name			Melting point, °C	Boiling point, °C	Density d_4^{20}
	trivial	Geneva	according to carbinol system			
CH_3OH	Methyl or wood alcohol	Methanol	Carbinol	−97.8	64.7	0.7924
CH_3-CH_2OH	Ethyl or grain alcohol	Ethanol	Methylcarbinol	−117.3	78.5	0.789
$CH_3-CH_2-CH_2OH$	Primary propyl alcohol	1-Propanol	Ethylcarbinol	−127	97.2	0.804
$CH_3-\underset{\displaystyle OH}{\underset{\vert}{CH}}-CH_3$	Secondary propyl alcohol or isopropyl alcohol	2-Propanol	Dimethylcarbinol	−88.5	82.3	0.785
$CH_3-CH_2-CH_2-CH_2OH$	Primary *n*-butyl alcohol	1-Butanol	*n*-Propylcarbinol	−89.5	117.7	0.8097
$CH_3-CH_2-\underset{\displaystyle OH}{\underset{\vert}{CH}}-CH_3$	Secondary *n*-butyl alcohol	2-Butanol	Methylethylcarbinol	−114.7	100	0.808
$CH_3-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_2OH$	Primary isobutyl alcohol	2-Methyl-1-propanol	Isopropylcarbinol	−108	108.4	0.801
$CH_3-\underset{\displaystyle OH}{\underset{\vert}{\overset{\displaystyle CH_3}{\overset{\vert}{C}}}}-CH_3$	Tertiary butyl alcohol	2-Methyl-2-propanol	Trimethylcarbinol	+25.5	83	0.788

$CH_3-CH_2-CH_2-CH_2-CH_2OH$	Primary *n*-amyl alcohol	1-Pentanol	*n*-Butylcarbinol	−78.5	138.0	0.814
$CH_3-CH_2-CH_2-CH(OH)-CH_3$	Secondary *n*-amyl alcohol	2-Pentanol	Methyl-*n*-propyl-carbinol	—	119.3	0.809
$CH_3-CH_2-CH(OH)-CH_2-CH_3$	Secondary *n*-amyl alcohol	3-Pentanol	Diethylcarbinol	—	115.6	0.821
$CH_3-C(CH_3)(OH)-CH_2-CH_3$	Tertiary amyl alcohol	2-Methyl-2-butanol	Dimethylethyl-carbinol	−11.9; −8.4	101.8	0.809
$CH_3-CH(CH_3)-CH_2-CH_2OH$	Isoamyl alcohol	3-Methyl-1-butanol	Isobutylcarbinol	−117.2	130.5	0.812
$CH_3-CH(CH_3)-CH(OH)-CH_3$	Secondary isoamyl alcohol	3-Methyl-2-butanol	Methylisopropyl-carbinol	—	114.0	0.819
$CH_3-CH(CH_2OH)-CH_2-CH_3$	Optically active amyl alcohol	2-Methyl-1-butanol	*sec*-*n*-Butylcarbinol	—	128.0	0.816
$CH_3-C(CH_3)_2-CH_2OH$	Neopentyl alcohol	2,2-Dimethyl-1-propanol	*tert*-Butylcarbinol	+53	114.0	0.812
$CH_3-(CH_2)_4-CH_2OH$	*n*-Hexyl alcohol	1-Hexanol	*n*-Amylcarbinol	−51.6	157.2	0.819

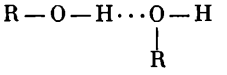
From a comparison of the boiling points of alcohols of similar structure, say, primary alcohols with a normal skeleton, it follows that in going from one member to another, similar member in the homologous series the boiling point increases by about 20°C. Branching raises the melting point (especially for tertiary alcohols, in which the branching starts from the functional group) and decreases the boiling point, just as in the case of hydrocarbons. As compared with hydrocarbons, alcohols boil at a very high temperature. For example, *n*-butane boils at —0.5°C, whereas *n*-butyl alcohol does so at 117.7°C.

Hydroxyl-containing compounds generally have anomalously high boiling points. This becomes clear from a comparison of the boiling points of the hydrogen compounds of oxygen and its neighbours in the Periodic System:

NH_3	H_2O	HF
(−33.3°C)	(100°C)	(19.5°C)
	H_2S	
	(−60.7°C)	

This is accounted for by the fact that water is an associated liquid and its molecules in the liquid phase have, on an average, a tripled molecular weight, $(H_2O)_3$. This gives rise to the numerous anomalies of water. Of its neighbouring hydrogen compounds only HF is associated in the liquid state, though to a lesser degree.

Alcohols and all organic hydroxyl-containing compounds are also associated, though less than water, and they also exhibit certain similar anomalies. Hence their high boiling points. Association is due to the formation of bonds of the type of electrostatic dipole attractions between the hydroxyl hydrogen, which is the positive end of the dipole, and the oxygen of the second alcohol molecule, which bears a partial negative charge. Such a bond is called **hydrogen bonding** and is denoted by three dots:

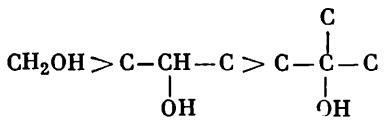


Hydrogen bonds are much weaker than the ordinary chemical bonds, which can be illustrated by comparing the average heats of bond formation (in kcal/mole):

C—C	82.6	O—H	110
C—H	98.7	—H . . . O<	*ca.* 6
C—O	85.5		

The smaller the number of alkyl groups that surround the hydroxyl, the greater is the opportunity for association through hydrogen bonding and the higher is the boiling point of the compound.

Therefore, primary alcohols boil higher than the isomeric secondary alcohols, and these again higher than the corresponding tertiary compounds:



The melting points are the highest, as is always the case, for compounds having a most symmetric structure: tertiary alcohols melt at higher temperatures than their isomers.

Methanol, ethanol and both propyl alcohols are miscible with water in all proportions, whereas butanol has a limited solubility (about 10 per cent) and amyl alcohols are insoluble. In aqueous solutions of alcohols, hydrogen bonding is formed between the hydrogen of water and the hydroxyl oxygen of alcohols. Thus, solutions of ethanol in water have anomalies of their own (the disturbance of density additivity, etc.).

(b) *Preparation of Alcohols*

General Methods of Synthesis. 1. *Hydrolysis of the halogen derivatives* (see page 102).

2. *Hydrogenation of carbon monoxide.* Depending on the reaction conditions, it is possible to prepare either methyl alcohol (methanol):

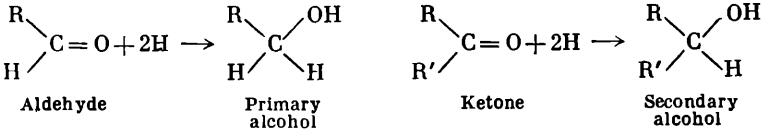
$$CO + 2H_2 \longrightarrow CH_3OH \qquad \Delta H = -216 \text{ kcal}$$

or a mixture of its primary homologues, beginning with ethyl alcohol (synthol).

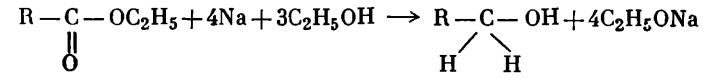
Large quantities of methanol are produced by hydrogenation of carbon monoxide with hydrogen at about 400°C and 200 kg/cm² over a catalyst which is a mixture of chromium oxide and zinc oxide.

The catalyst used in the production of synthol consists of iron and cobalt and the process is conducted under a pressure of several tens of atmospheres at elevated temperature. The process can be made to proceed in the direction of predominant formation of a mixture of primary propyl and isobutyl alcohols.

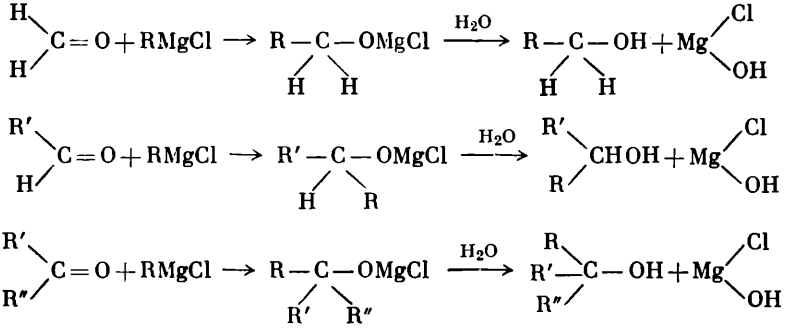
3. *Reduction of aldehydes and ketones.* The reduction is effected by the use of hydrogen in the presence of catalysts (Ni, Pt). Other reducing agents may also be employed. In this way, aldehydes give primary alcohols and ketones, secondary alcohols:



4. *Reduction of carboxylic acids and their derivatives.* Particularly popular is the reduction of esters of carboxylic acids by the action of metallic sodium in boiling alcohol (the Bouveault-Blanc method):



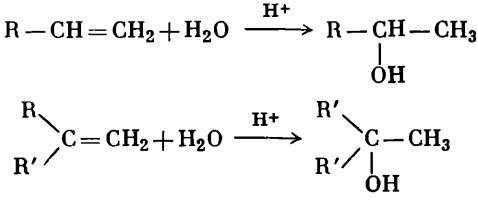
5. *Addition of organometallic compounds to carbonyl compounds.* Organomagnesium compounds (Grignard reagents) and also organolithium, organozinc and, often, organosodium compounds are added:



First, an organometallic compound adds on to an aldehyde or a ketone, and after the adduct is decomposed by water there is formed an alcohol and a basic magnesium salt.

Thus, organometallic synthesis makes it possible to produce primary, secondary and tertiary alcohols. For primary alcohols to be synthesized, an organomagnesium compound (*a Grignard reagent*) is allowed to react with formaldehyde; secondary alcohols are prepared by the reaction between aldehydes (other than formaldehyde) and Grignard reagents; and tertiary alcohols are produced by using ketones.

6. *Hydration of olefins in the presence of acids.* Depending on the structure of the olefin, either secondary or tertiary alcohols are formed (from primary alcohols only ethanol, R=H, can be produced in this way):



First, the hydrogen ion attacks that carbon atom which carries a larger number of hydrogen atoms and which is therefore more electronegative than the neighbouring carbon (Markovnikov's rule; for more detail, see page 336). Then water adds on to the adjacent carbon, this being accompanied by the expulsion of H^+. This method is employed on an industrial scale for producing ethyl, *sec*-propyl and *tert*-butyl alcohols.

7. *Fermentation of sugars.* Some sugars (glucose, fructose, maltose, and also saccharose after it has been hydrolysed) are subjected to fermentation with yeast. The summary equation for the conversion of sugars into ethyl alcohol and carbon dioxide on fermentation is as follows:

$$C_6H_{12}O_6 \longrightarrow 2C_2H_5OH + 2CO_2$$

This equation provides no information on the mechanism of the reaction, which will be discussed after the study of the structure of sugars.

Yeasts are unicellular plant microorganisms (included in the broad classification of the fungi). Fermentation is caused by the enzymes present in yeast, which are collectively called **zymase.** Zymase is soluble in water and can be extracted from dried yeast by water (A. N. Lebedev). Yeast can be compressed and a solution of zymase in the cell juice obtained (E. Buchner). In both cases the zymase solution containing no living cells causes fermentation—a catalytic multistage decomposition of sugar into alcohols and carbon dioxide. The role played by zymase is purely that of a catalyst.

The process of fermentation has long been known in viniculture. The juice pressed from grapes is subjected to fermentation. No yeast is specially added since it is present on grape peels, and therefore seeding with raisins, for example, in preparing a fermented drink (kvass), is tantamount to adding yeast. The grape juice contains glucose which undergoes fermentation. Fermentation produces an aqueous solution of alcohol (wine) not stronger than 12-14° (the volume per cent of ethanol) since the ethanol hinders the activity of yeast enzymes. Stronger and, especially, sweet wines (dessert wines) are produced by "fortifying": when not all the glucose has been fermented in the high-sugar-content juice, ethanol is added—fermentation is arrested and part of the glucose is retained.

Alcohol is produced by using cheaper sources of sugar compounds—starch (corn, potatoes, etc.) or wood. In the former case, the tubers of potatoes (or grains) are heated with water at a temperature above 100°C under pressure and then the pressure is rapidly released. A paste is obtained, to which sugar is added. For this purpose, use is made of malt or special microorganisms which saccharify the starch. Malt is dried and ground germinated grain (usually, barley grain), which has collected enzymes required for the plant to activate the

stored starch — its transformation into a soluble carbohydrate, maltose. Malt usually contains a very large amount of enzymes called diastase. At a temperature of about 60°C the paste becomes saccharized by diastase into maltose, following which yeast is added to induce fermentation. The aqueous-alcoholic solution obtained is distilled off and subjected to fractionation to produce alcohol of desired proof, but not above 96° (about 96 per cent of ethanol and 4 per cent of water form a constant-boiling mixture or **azeotrope** which boils at 78.15°C).

Absolute alcohol (anhydrous ethanol) is produced by removing the water from "96%" alcohol by chemical means. To this end, CaO or anhydrous $CuSO_4$ is added first, and then metallic calcium is introduced. Benzene may be added to absolute alcohol to remove the water, in which case a ternary azeotrope containing water, alcohol and benzene and having a minimum boiling point is distilled off; then the remaining mixture of ethanol and benzene, which forms no azeotrope and can be separated by fractional distillation, is subjected to fractionation.

To maintain the activity of yeast, ammonium salts must be added as a source of nitrogen. When yeast grows and increases in mass, it converts ammonium salts into amino acids (see Volume II) and proteins. During the fermentation, a certain part of amino acids loses its carboxyl group as CO_2 and by exchanging the NH_2 group for a hydroxyl group is converted into an alcohol. In this way, the spirits of **fusel oil** are produced, which are primary alcohols:

Propyl alcohol . . . . . $CH_3-CH_2-CH_2OH$

Isobutyl alcohol (2-methyl-1-propanol) . . . . . $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2OH$

Isoamyl alcohol (3-methyl-4-butanol) . . . . . $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_2OH$

Optically active amyl alcohol (2-methyl-1-butanol) . . . . . $C_2H_5-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2OH$

(c) *Chemical Properties of Alcohols*

All alcohols have a number of chemical properties in common; but there are reactions which proceed differently for primary, secondary and tertiary alcohols. We shall first consider those reactions which are common to all alcohols.

1. *Formation and properties of metal alkoxides.* When alcohols are acted on by alkali metals, say, sodium, the reaction that takes

place, though less vigorous, is similar to the reaction between sodium and water (see also page 23):

$$2ROH + 2Na \longrightarrow 2RONa + H_2$$
$$2HOH + 2Na \longrightarrow 2HONa + H_2$$

Such metallic derivatives of alcohols are collectively called **alkoxides** (e.g., sodium methoxide, CH_3ONa; sodium ethoxide, C_2H_5ONa; propoxide). They are also known as **alcoholates** (for example, sodium methylate, CH_3ONa; sodium ethylate, C_2H_5ONa; propylate).

Alkoxides of metals other than alkali are also known, but they are prepared indirectly. For example, alkaline-earth metals do not react directly with alcohols. But the alkoxides of alkaline-earth metals and also of Mg, Zn, Cd, Al and other metals which form reactive organometallic compounds can be obtained by the action of an alcohol on such organometallic compounds. For example,

$$2CH_3OH + Zn(CH_3)_2 \longrightarrow (CH_3O)_2Zn + 2CH_4$$

Mixed alkoxide-bromides can also be synthesized:

$$CH_3CH_2OH + CH_3MgBr \longrightarrow CH_3CH_2OMgBr + CH_4$$

Furthermore, alkoxides can be prepared by an interchange reaction between a sodium alkoxide and a metal chloride in a nonaqueous solution:

$$3CH_3ONa + AlCl_3 \longrightarrow (CH_3O)_3Al + 3NaCl$$

The alkoxides of alkali metals are compounds with a strongly polar bond (the O—Me bond), which undergo electrolytic dissociation in solution in a corresponding alcohol with the formation of an *alkoxide ion* (methoxide, ethoxide, propoxide ions, etc.):

$$CH_3ONa \longrightarrow CH_3O^- + Na^+$$

Water is a stronger acid than alcohols. The dissociation constant of water is $K_a = 10^{-16}$, that of methanol is about 10^{-17}, and the dissociation constants of ethanol and other primary alcohols are about 10^{-18} (i.e., by two orders of magnitude lower than the dissociation constant of water); secondary and, notably, tertiary alcohols are even weaker acids. It is for this reason that the action of water on alkoxides leads to an equilibrium strongly displaced to the right:

$$C_2H_5ONa + H_2O \rightleftarrows C_2H_5OH + NaOH$$

or, in an ionic form,

$$C_2H_5O^- + H_2O \rightleftarrows C_2H_5OH + OH^-$$

Alkoxide ions bind a hydrogen ion more completely than hydroxyl ions since a less strongly dissociated alcohol molecule is formed. Therefore the alkoxides of alkali metals are even stronger bases than sodium hydroxide or potassium hydroxide. Particularly strong

bases are the alkoxides of the least dissociated tertiary alcohols, say, $(CH_3)_3CONa$.

An alcoholic solution of sodium hydroxide is a stronger base than its aqueous solution just because it contains a sodium alkoxide formed as a result of an equilibrium reaction:

$$ROH + NaOH \rightleftarrows RONa + H_2O$$

The alkoxides of alkali metals are solids which when heated decompose without melting. Aluminium alkoxides can be distilled since they have no typical ionic metal-alkoxy bond.

2. *Formation of esters (esterification reaction).* When oxygen-containing mineral and organic acids are reacted with alcohols, there takes place a reaction which may be represented by the following examples:

$$ROH + \begin{matrix} HO \\ HO \end{matrix}\!\!>\!SO_2 \rightleftarrows \begin{matrix} RO \\ HO \end{matrix}\!\!>\!SO_2 + H_2O$$

$$2ROH + \begin{matrix} HO \\ HO \end{matrix}\!\!>\!SO_2 \rightleftarrows \begin{matrix} RO \\ RO \end{matrix}\!\!>\!SO_2 + 2H_2O$$

$$ROH + HONO_2 \rightleftarrows RO-NO_2 + H_2O$$

$$ROH + HO-\overset{\overset{O}{\|}}{C}-CH_3 \rightleftarrows RO-\overset{\overset{O}{\|}}{C}-CH_3 + H_2O$$

Such an interaction between alcohols and acids is known as **esterification,** and the compounds obtained are called **esters.** The equation of this reaction bears an outer resemblance to that of neutralization of alkali by an acid:

$$NaOH + HO-\overset{\overset{O}{\|}}{C}-CH_3 \longrightarrow NaO-\overset{\overset{O}{\|}}{C}-CH_3 + H_2O$$

But there is a significant difference between these reactions. Neutralization is an ionic reaction and proceeds instantaneously; it is essentially an interaction between ions:

$$H^+ + OH^- \longrightarrow H_2O$$

The esterification reaction proceeds in a different way. In most cases, alcohols react, giving up not the hydroxyl (as an alkali on neutralization) but the hydrogen of the hydroxyl group; acids (organic and some mineral acids, but not all) lose their hydroxyl groups. This mechanism has been established with the aid of an alcohol labelled with an oxygen isotope, ^{18}O. As has been found, the interaction of such an alcohol with acids RCOOH results in the formation of ordinary water and not of $H_2{}^{18}O$.

3. *Formation of esters by the action of acid chlorides of inorganic and organic acids on alcohols.* This may be exemplified by the following reactions of acid chlorides with primary alcohols:

$$ROH + ClN{=}O \longrightarrow RO{-}N{=}O + HCl$$
$$3ROH + BCl_3 \longrightarrow (RO)_3B + 3HCl$$
$$3ROH + PCl_3 \longrightarrow (RO)_3P + 3HCl$$
$$ROH + Cl{-}\overset{\overset{O}{\|}}{C}{-}CH_3 \longrightarrow RO{-}\overset{\overset{O}{\|}}{C}{-}CH_3 + HCl$$
$$ROH + Cl{-}\overset{\overset{O}{\|}}{C}{-}Cl \longrightarrow RO{-}\overset{\overset{O}{\|}}{C}{-}Cl + HCl$$

When inorganic acid halides are reacted with tertiary and secondary alcohols, the hydroxyl group is replaced by halogen:

$$3(CH_3)_3COH + PBr_3 \longrightarrow 3(CH_3)_3CBr + P(OH)_3$$

The exchange of the hydroxyl for a halogen also occurs when primary alcohols are acted on by PBr_3 or PI_3:

$$3C_2H_5OH + PBr_3 \longrightarrow 3C_2H_5Br + P(OH)_3$$

4. *Dehydration of alcohols to olefins.* All alcohols (except methyl alcohol) lose the elements of water to form olefins when their vapour is passed over aluminium oxide heated to about 375°C:

$$CH_3{-}CH_2OH \xrightarrow{Al_2O_3} CH_2{=}CH_2 + H_2O$$

Water is especially readily eliminated from tertiary alcohols.

Olefins are also formed when alcohols are heated with acids such as oxalic and phthalic and also with sulphuric acid. In such reactions, an ester is first formed, which decomposes into an acid and an olefin when heated to a high temperature (see page 334).

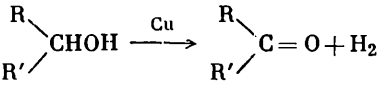
5. *Dehydrogenation and oxidation.* Primary, secondary and tertiary alcohols differ in their behaviour on dehydrogenation and oxidation and can thereby be distinguished from one another.

When the vapour of a primary or a secondary alcohol (but not a tertiary one) is passed over metallic copper at elevated temperature, two hydrogen atoms are split off and the primary alcohol is converted into an aldehyde*:

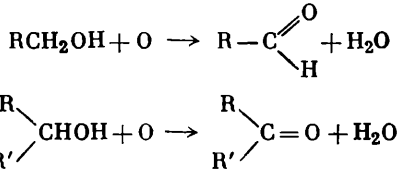
$$RCH_2OH \xrightarrow{Cu} R{-}\overset{\overset{O}{\diagup\!\!\diagup}}{C}{\diagdown}H + H_2$$

* Hence the name aldehyde, from *alcohol dehydrogenation.*

Secondary alcohols yield ketones under these conditions:



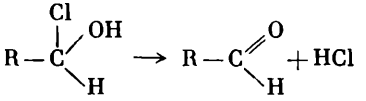
The behaviour of primary and secondary alcohols on oxidation is also characteristic, allowing one to distinguish between the two types of alcohol. They may be oxidized either by the wet method, for example, by the action of chromic acid, or catalytically, using metallic copper as a catalyst and the oxygen of the air as an oxidizing agent:



A similar oxidation reaction takes place when alcohols are allowed to react with halogens in alkaline medium, but the resulting aldehyde or ketone undergoes further halogenation at the carbon atom nearest to the carbonyl group.

(d) *Halogen-Substituted Alcohols* (*Halohydrins*)

A halogen and a hydroxyl attached to the same carbon atom form an unstable grouping, and such substituted alcohols decompose instantaneously:



Thus, no halogen derivatives of methanol exist. The simplest halogen-substituted alcohol of ethanol is β-chloroethanol or **ethylenechlorohydrin**, $ClCH_2—CH_2OH$. It is made from ethylene to which chlorine is added in aqueous solution (for more detail, see page 338):

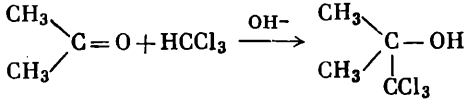
$$CH_2=CH_2+Cl_2+H_2O \longrightarrow ClCH_2CH_2OH+HCl$$

β-Trichloroethanol, $CCl_3—CH_2OH$, can be prepared from $CCl_3—CHO$ (chloral) and isopropyl alcohol in the presence of aluminium isopropoxide, $Al[OCH(CH_3)_2]_3$, by the Meerwein-Ponndorf reaction (see page 172).

β-Tribromoethanol (the trivial name is **avertin**), produced in an analogous way, is used medicinally in the form of a solution in *tert*-amyl alcohol as a rectal anesthetic in surgical operations. β-

Trifluoroethanol is interesting by being a rather strong acid (pK_a = = 12.4 in water). The *acidifying* action of the halogens, in particular fluorine, will be discussed on page 244.

The condensation of acetone with chloroform in the presence of alkali gives trichloro-*tert*-butyl alcohol, or **chloretone** (Willgerodt reaction):



(c) *Uses of Alcohols*

Methyl and ethyl alcohols and fusel oil have long served as raw materials for production of acyclic (fatty) compounds. At present, the major proportion of organic raw materials is supplied by the petrochemical industry, in particular, in the form of olefins and paraffinic hydrocarbons.

Methanol, ethanol and the higher alcohols are used as such and in the form of acetic esters as solvents, and the higher alcohols, beginning with butyl alcohol, are used as the esters of phthalic, sebacic and other dihydric acids as plasticizers.

Monohydric alcohols are used in the various organic syntheses for introducing corresponding alkyl groups, for which purpose alcohols are first converted into alkyl halides and then, if necessary, into organomagnesium compounds.

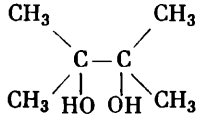
Large quantities of methanol are converted by the action of atmospheric oxygen into the corresponding aldehyde—formaldehyde which has found numerous applications. Methanol is a toxic substance, and when ingested can cause blindness and death (the lethal dose is about 30 g). Higher alcohols are not too toxic.

One of the major industrial uses of ethanol until recently has been in the production of butadiene (the Lebedev process) and synthetic rubber. Considerable amounts of ethanol are used for production of the various alcoholic beverages.

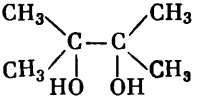
B. Dihydric Alcohols or Glycols (Alkanediols)

The dihydric derivatives of alkanes (discovered by Wurtz) are known as **glycols** or **alkanediols** (or, simply, *diols*). The hydroxyl groups in alkanediols are attached to two different carbon atoms which may be either adjacent to (vicinal glycols) or remote from each other. 1,2-Glycols are sweet-tasting liquids (hence the name of the class). Lower glycols are viscous water-miscible liquids of higher density than monohydric alcohols. They boil at a high temperature (see Table 2.8).

TABLE 2.8. **Glycols**

Formula	Name		Melting point, °C	Boiling point, °C	Density d_4^{20}
	trivial	Geneva			
$HOCH_2-CH_2OH$	Ethylene glycol	1,2-Ethanediol	−17.4	197.2	1.1155
$CH_3-CH(OH)-CH_2OH$	Propylene glycol	1,2-Propanediol	—	189	1.040
$HOCH_2-CH_2-CH_2OH$	Trimethylene glycol	1,3-Propanediol	—	214 (dec.)	1.0597
$HOCH_2-CH_2-CH_2-CH_2OH$	Tetramethylene glycol	1,4-Butanediol	+16	230	1.020
	Tetramethylethylene glycol or pinacol	2,3-Dimethyl-2,3-butanediol	38	172.8	0.9672 (at 15°C)

The most important glycols are 1,2-ethanediol, or ethylene glycol; 1,2-propanediol; 1,4-butanediol; and **pinacols** (symmetrically built ditertiary glycols with hydroxyl groups being on contiguous carbon atoms), the simplest member being 2,3-dimethyl-2,3-butanediol:



Pinacol

Glycols with a short carbon chain, and primarily ethylene glycol, are insoluble in hydrocarbons and ether but are miscible with water and alcohols; as solvents they are closer to water and methanol than to ordinary organic solvents.

(a) *Preparation of Glycols*

In principle, glycols can be made by all the synthetic methods used for preparation of alcohols.

1. Hydrolysis of halogen derivatives:

$$ClCH_2-CH_2Cl+2H_2O \longrightarrow HOCH_2-CH_2OH+2HCl$$

or

$$ClCH_2-CH_2OH+H_2O \longrightarrow HOCH_2-CH_2OH+HCl$$

2. Reduction of esters of dibasic acids by the Bouveault-Blanc procedure (page 128):

$$C_2H_5O-\overset{\overset{O}{\|}}{C}-(CH_2)_n-\overset{\overset{O}{\|}}{C}-OC_2H_5+8Na+6C_2H_5OH \longrightarrow$$

$$\longrightarrow HOC-(CH_2)_n-COH+8C_2H_5ONa$$

3. The most important are the methods of preparing 1,2-glycols from olefins. In the laboratory, the oxidation of an olefin with an aqueous solution of $KMnO_4$ can be accomplished (the Wagner reaction). In this reaction, a hydroxyl group adds on to each of the two carbon atoms linked by a double bond:

$$3CH_2=CH_2+4H_2O+2KMnO_4 \longrightarrow 3HOCH_2-CH_2OH+2KOH+2MnO_2$$

If the olefin is cyclic, the addition takes place in the *cis*-position.

4. Preparation of glycols via chlorohydrins. When chlorine and water are reacted with an olefin, a chlorohydrin can be obtained (see pages 134 and 338), say, $ClCH_2-CH_2OH$. The chlorohydrin can be converted either directly into a glycol by hydrolysis (see above) or first into an olefin oxide by the action of quicklime and then into a glycol by acid hydrolysis:

$$ClCH_2-CH_2OH+Ca(OH)_2 \longrightarrow H_2C\!-\!CH_2+CaCl_2+2H_2O \quad (O)$$

$$H_2C\!-\!CH_2+H_2O \xrightarrow{H^+} HOCH_2-CH_2OH \quad (O)$$

5. Pinacols are produced by the reduction (incomplete) of ketones either electrochemically or by the action of magnesium in the presence of iodine:

$$2\ (CH_3)_2C=O+2Mg+I_2 \longrightarrow (CH_3)_2C(OMgI)-C(OMgI)(CH_3)_2 \xrightarrow{2H_2O} (CH_3)_2C(OH)-C(OH)(CH_3)_2$$

6. 1,4-Butanediol (a valuable product which is an intermediate in the production of butadiene and synthetic rubber) is made on an

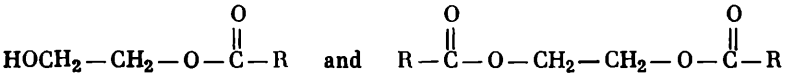
industrial scale by hydrogenation of 1,4-butynediol ($HOH_2C-C\equiv C-CH_2OH$); the latter is prepared from acetylene and formaldehyde (see page 364).

(b) *Chemical Properties of Glycols*

Like monohydric alcohols, glycols may have primary, secondary and tertiary hydroxyl groups. Ethylene glycol is a di-primary, propylene glycol a primary-secondary, and pinacol a di-tertiary alcohol. All that has been said about the properties of primary, secondary, and tertiary alcohols also refers to the corresponding glycols.

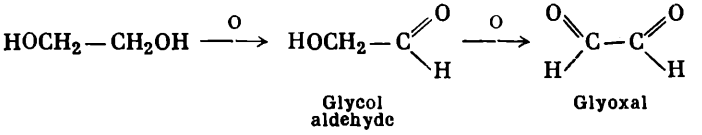
1. Glycols readily form chlorohydrins and bromohydrins when reacted with HCl and HBr, but the second hydroxyl group is replaced by halogen more difficultly (more readily by the action of PCl_5 or $SOCl_2$).

2. When acted on by acids, glycols give two series of esters:

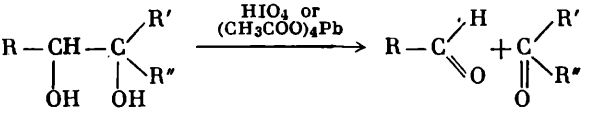


The ethers of glycols will be discussed later in a separate section.

3. The oxidation of primary glycols results in the formation of aldehydes. For example, when ethylene glycol is oxidized, glyoxal is obtained:



The oxidation of 1,2-diols by periodic acid (Malaprade) or by lead tetraacetate (Criegee)* leads to the fission of the bond between the hydroxyl-bearing carbon atom and to the conversion of each of them into an aldehyde (or ketonic) group:



This method is very important for the elucidation of the structure of 1,2-glycols.

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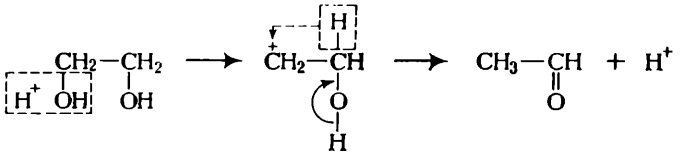
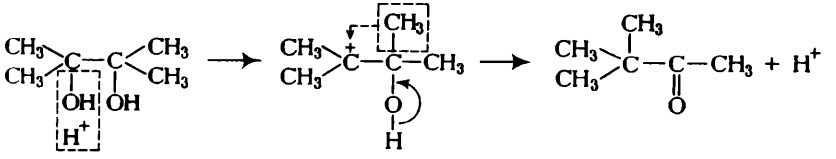
* These two highly selective reagents are called *glycol-splitting* (or *-cleaving*) *agents* to distinguish them from other oxidizing agents.—*Tr.*

4. The dehydration of glycols (by acids or zinc chloride) leads to the formation of aldehydes (or ketones). By analogy with the pinacol rearrangement (see below), it is believed that the mechanism of this dehydration reaction consists in that a carbonium ion is first formed by the removal of one hydroxyl group by a proton and then the hydrogen atom with its electron pair (in the form of a hydride ion) migrates to the carbonium ion carbon (**hydride transfer**):

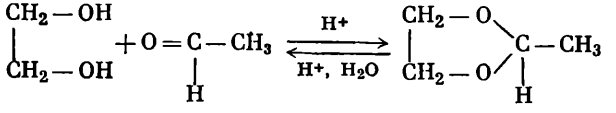


When pinacols are dehydrated, not a hydrogen but a methyl group migrates to the electron-deficient carbon atom of the carbonium ion and the **pinacol rearrangement** (also known as the **pinacol-pinacolone rearrangement**) takes place (see Volume IV, "Rearrangements"), which is accompanied by a change of the carbon skeleton:



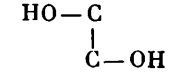
Pinacol Pinacolone

5. Aldehydes in acid solution *acetylate* 1,2-glycols to form cyclic acetals (it is in acid and not in alkaline solution that the hydrolysis of the acetal regenerates the starting compounds):



1,3-Glycols are capable of reacting in a similar manner, giving six-membered cyclic acetals.

For acetal formation reactions to be effected, it is necessary that both hydroxyl groups lie in one plane, i.e., rotate freely about the carbon-carbon bond:



This condition is fulfilled by open-chain glycols; cyclic glycols do not always meet this requirement.

Ethylene glycol and propylene glycol are used as antifreezing compounds. They are mixed with water to prevent freezing in radiators of motor cars because such mixtures do not freeze in winter time. Ethylene glycol is also used for production of solvents such as dioxan and carbitol (see Sec. 2.5). The ester formed by ethylene glycol and nitric acid (glycol dinitrate) is an explosive.

C. Polyhydric Alcohols

Trihydric Alcohols (Alkanetriols). The only important representative of trihydric alcohols (triols) is glycerine or glycerol (1,2,3-propanetriol). This compound was discovered by Scheele and studied by Chevreul, Pelouze, Berthelot, and Wurtz. Glycerol is a highly viscous colourless syrup of sweet taste (from which it derives its name); m.p. 17°C, b.p. 290°C.

Glycerol is prepared by the hydrolysis of fats which are the esters of glycerol and the higher homologues of acetic acid (and of their olefinic isologues). When fats are hydrolysed by superheated steam, glycerol remains in aqueous solution, which is separated from the layer of molten fatty acids; when water is distilled off from this solution, glycerol can be isolated.

Glycerol is also formed in small amounts in the fermentation of sugars

At present, glycerol is synthesized on an industrial scale from propylene (propene) which is isolated from the gases formed in the cracking of petroleum. This synthesis is a proof of the structure of glycerol as propanetriol.

The first stage is the chlorination of propylene at a high temperature (500°C) resulting in the formation of allyl chloride which retains the double bond (the L'vov reaction):

$$\underset{\text{Propylene}}{CH_2=CH-CH_3}+Cl_2 \longrightarrow \underset{\text{Allyl chloride}}{CH_2=CH-CH_2Cl}+HCl$$

This is followed by the addition of chlorine and water, as a result of which allyl chloride is converted into 1,3-dichloro-2-propanol:

$$CH_2=CH-CH_2Cl+Cl_2+H_2O \longrightarrow \overset{Cl}{\overset{|}{CH_2}}-\overset{OH}{\overset{|}{CH}}-\overset{Cl}{\overset{|}{CH_2}}+HCl$$

which is then hydrolysed to give glycerol:

$$\underset{\text{1,3-Dichloro-2-propanol}}{\overset{Cl}{\overset{|}{CH_2}}-\overset{OH}{\overset{|}{CH}}-\overset{Cl}{\overset{|}{CH_2}}}+2H_2O \longrightarrow \underset{\text{1,2,3-Propanetriol (glycerol)}}{\overset{OH}{\overset{|}{CH_2}}-\overset{OH}{\overset{|}{CH}}-\overset{OH}{\overset{|}{CH_2}}}+2HCl$$

The first synthesis of glycerol (Friedel and Silva, 1872) is similar to the one just described, with the only difference that propylene

was chlorinated in the cold and the final addition product was 1,2-dichloropropane:

$$CH_2=CH-CH_3+Cl_2 \longrightarrow \underset{Cl}{\overset{|}{CH_2}}-\underset{Cl}{\overset{|}{CH}}-CH_3$$

1,2-Dichloropropane was then chlorinated by way of a substitution reaction to 1,2,3-trichloropropane:

$$\underset{Cl}{\overset{|}{CH_2}}-\underset{Cl}{\overset{|}{CH}}-CH_3+Cl_2 \longrightarrow \underset{Cl}{\overset{|}{CH_2}}-\underset{Cl}{\overset{|}{CH}}-\underset{Cl}{\overset{|}{CH_2}}+HCl$$

which is converted on hydrolysis into glycerol.

A new and promising method of preparing glycerol has been worked out by the Polish chemists (Beresz and L. Jakubowicz). The raw material is propylene which is oxidized to acrolein—the simplest unsaturated aldehyde. The latter is reduced by isopropyl alcohol over a mixed catalyst (ZnO-MgO) to allyl alcohol which is hydroxylated into glycerol by hydrogen peroxide:

$$CH_3-CH=CH_2 \longrightarrow CH_2=CH-\overset{O}{\overset{\|}{C}}-H$$

$$CH_2=CH-\overset{O}{\overset{\|}{C}}-H+CH_3-\underset{OH}{\overset{|}{CH}}-CH_3 \xrightarrow{ZnO-MgO}$$

$$\longrightarrow CH_2=CH-CH_2OH+CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$

$$CH_2=CH-CH_2OH+H_2O_2 \longrightarrow \underset{OH}{\overset{|}{CH_2}}-\underset{OH}{\overset{|}{CH}}-CH_2OH$$

Isopropyl alcohol is also manufactured from propylene.

The reduction of acrolein by isopropyl alcohol is similar to the Oppenauer-Meerwein-Ponndorf reduction (see page 172). It is true, the latter reaction makes use of a different catalyst—aluminium isopropoxide. The resulting allyl alcohol formed is subjected to hydroxylation by the action of hydrogen peroxide to give glycerol. The scheme of the process is as follows:

$$HCHO+CH_3-\overset{O}{\overset{\|}{C}}-H \longrightarrow \left[HOCH_2-CH_2-\overset{O}{\overset{\|}{C}}-H\right] \xrightarrow[-H_2O]{} \underset{\text{Acrolein}}{CH_2=CH-\overset{O}{\overset{\|}{C}}-H}$$

$$CH_2=CH-\overset{O}{\overset{\|}{C}}-H+C_2H_5OH \xrightarrow{Al(OR)_3} CH_2=CH-CH_2OH+CH_3-\overset{O}{\overset{\|}{C}}-H$$

Allyl alcohol

$$CH_2=CH-CH_2OH+H_2O_2 \longrightarrow \underset{\text{Glycerol}}{\underset{OH}{\overset{|}{CH_2}}-\underset{OH}{\overset{|}{CH}}-\underset{OH}{\overset{|}{CH_2}}}$$

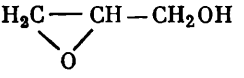
In another technically convenient method of producing glycerol, the starting material is glucose. The hydrogenation of glucose over nickel and other catalysts involves simultaneously the reduction of the aldehyde group and the cleavage of the $C_3—C_4$ bond and yields two molecules of glycerol:

$$CH_2OH—CHOH—CHOH—CHOH—CHOH—CHO \xrightarrow{H_2}$$
$$\rightarrow CH_2OH—CHOH—CHOH—CHOH—CHOH—CH_2OH \xrightarrow{H_2}$$
$$\rightarrow 2CH_2OH—CHOH—CH_2OH$$

The by-products formed in this reaction (due to the rupture of the $C_2—C_3$ bond) is a certain amount of ethylene glycol and threitol—a stereoisomer of erythritol.

Not only glucose but also polysaccharides containing glucose linkages (e.g., cheap cellulose) can be subjected to hydrogenation.

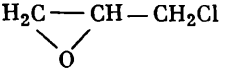
Glycerol gives with acids three series of esters: mono-, di-, and triesters. The first two types of compounds may have isomers: the products of esterification at primary and secondary groups. The action of HCl on glycerol yields a mixture of two monochlorohydrins of glycerol, which contains α-monochlorohydrin, $CH_2OH—CHOH—CH_2Cl$ (3-chloro-1,2-propanediol), and β-monochlorohydrin, $CH_2OH—CHCl—CH_2OH$ (2-chloro-1,3-propanediol), the former being present in a greater amount than the latter. The alkali treatment of either of the two isomers gives the same compound—glycidol:



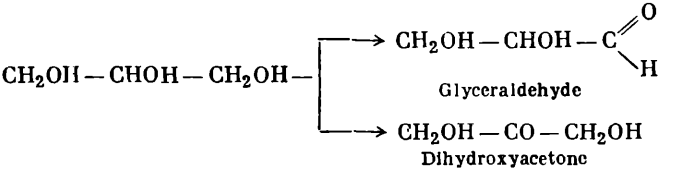
When glycerol is treated with hydrogen chloride under more drastic conditions, two dichlorohydrins result:

$$CH_2Cl—CHOH—CH_2Cl \qquad CH_2OH—CHCl—CH_2Cl$$

which when treated with alkali give **glycerol epichlorohydrin**



Being both a primary and a secondary alcohol, glycerol, which has found many uses in organic synthesis, forms on oxidation a mixture of the corresponding aldehyde and ketone:

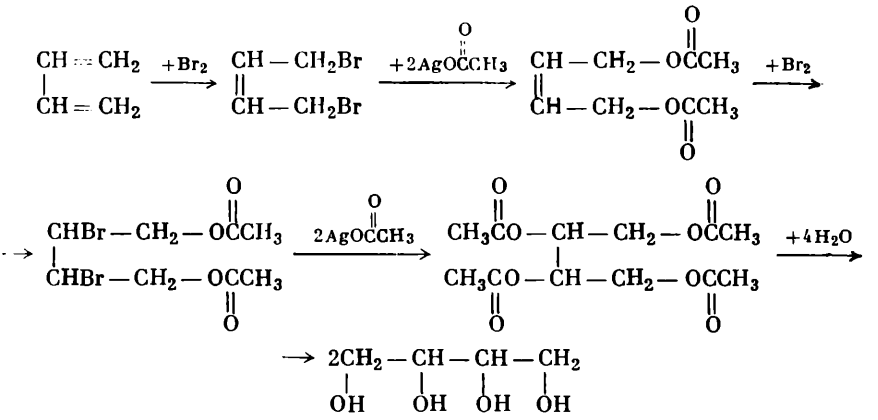


These compounds will be encountered in our study of sugars with which they are closely related.

Dihydroxyacetone can be made by the chlorination of acetone to 1,3-dichloroacetone, $ClCH_2—CO—CH_2Cl$, and by hydrolysis of the latter. This reaction also proves the structure of glycerol.

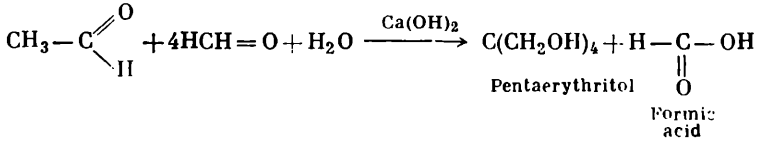
Glycerol is extensively used as a softening agent, particularly in perfumery. It is also used to impart a high consistency and a sweet taste to liquors. Large quantities of glycerol are used for the manufacture of nitroglycerine employed in dynamites and smokeless powders (see page 149), and for the production of epoxy (via epichlorohydrin) and glyphthalic resins used as a base for lacquers and varnishes.

Tetrahydric, Pentahydric and Hexahydric Alcohols (Erythritols, Pentitols and Hexitols). A representative of the tetrahydric alcohols is **erythritol** (1,2,3,4-butanetetraol) which is found in the free state in nature and in the form of esters in lichens and in some algae. The synthetic tetrahydric alcohol erythritol has been obtained from butadiene, $CH_2=CH—CH=CH_2$, as follows:



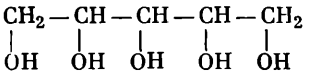
Stereoisomeric erythritols are solid sweet-tasting substances which dissolve readily in water.

Pentaerythritol (tetrahydroxyneopentane), $C(CH_2OH)_4$ does not occur in nature. It is a high-melting solid (m.p. 262°C). It is produced synthetically by the interaction of formaldehyde and an aqueous solution of acetaldehyde in alkaline medium:

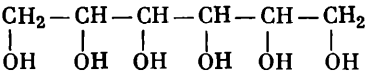


Pentaerythritol is nitrated to give its tetranitrate which is an extremely powerful explosive (PETN or penthrite, see page 149).

Pentitols and **hexitols**



Pentitol



Hexitol

are solid water-soluble sweet-tasting substances. There are many stereoisomers known for each of these alcohols. Some of the pentitols and hexitols are found in nature, say, *adonitol* (in *Adonis vernalis*), stereoisomeric hexitols such as mannitol, dulcitol, sorbitol, iditol. They all have a normal carbon skeleton and can be obtained by the reduction of the corresponding sugars which are their monoaldehydes.

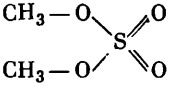
The stereochemistry of polyhydric alcohols and their relation to sugars will be treated in a separate section devoted to carbohydrates (Volume II).

2.4. Esters of Mineral Acids

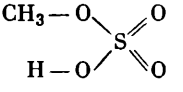
This class of compounds may be regarded formally as derivatives of acids, in which the acid hydrogen is replaced by alkyl (or, in general, carbon) radicals.

Polybasic acids give rise to two types of esters—**acid esters** and **neutral esters** (also called normal esters).

(a) Esters of sulphuric acid:

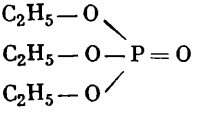


Neutral ester

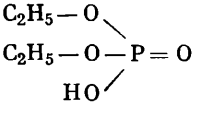


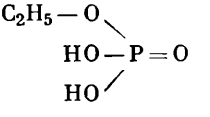
Acid ester

(b) Esters of phosphoric acid:



Neutral ester





Acid esters

In contrast to acids (and alcohols), neutral esters are completely undissociated compounds; acid esters are genuine acids (they are also known as ester-acids).

Esters are named either in descriptive terms—ethyl ester of nitric acid; acid methyl ester of sulphuric acid; neutral methyl ester of

sulphuric acid, or, briefly, just like salts—ethyl nitrate, methyl hydrogen sulphate, dimethyl sulphate. Methyl hydrogen sulphate and its ethyl homologue are also called methylsulphuric acid and ethylsulphuric acid.

It is interesting to trace the transition from ionic alkoxide derivatives of metals to undissociated neutral esters of oxy-acids. For this purpose, let us compare these compounds with the hydroxides of the corresponding elements of the Periodic System:

$LiOH$	$Be(OH)_2$	$B(OH)_3$	$CO(OH)_2$	$NO_2(OH)$		
$NaOH$	$Mg(OH)_2$	$Al(OH)_3$	$Si(OH)_4$	$PO(OH)_3$	$SO_2(OH)_2$	ClO_3OH
$LiOCH_3$	$Be(OCH_3)_2$	$B(OCH_3)_3$	$CO(OCH_3)_2$	$NO_2(OCH_3)$		
$NaOCH_3$	$Mg(OCH_3)_2$	$Al(OCH_3)_3$	$Si(OCH_3)_4$	$PO(OCH_3)_3$	$SO_2(OCH_3)_2$	ClO_3OCH_3

Formally, all the compounds of the lower two rows are the methylated (at the hydroxyl hydrogen) analogues of the compounds of the upper rows. Their properties, however, change considerably in going from left to right. For example, the alkoxides in the extreme left column are capable of electrolytic dissociation into the ions Me^+ and OCH_3^-, just as the corresponding hydroxides. The alkoxides in the medium columns do not dissociate into ions, but on hydrolysis the rupture of the element-oxygen bond is very likely to occur. The esters in the right columns are not capable of dissociation at all and undergo hydrolysis with rupture of the C—O bond in the alkoxyl group, the element-oxygen bond remaining intact. For example, on hydrolysis with heavy water the alkoxides give ordinary alcohols, whereas sulphates (phosphates) yield a heavy alcohol:

$$Mg(|OCH_3)_2 + 2H_2{}^{18}O \longrightarrow Mg(^{18}OH)_2 + 2CH_3OH$$
$$(CH_3|O)_2SO_2 + 2H_2{}^{18}O \longrightarrow H_2SO_4 + 2CH_3{}^{18}OH$$
$$(CH_3|O)_3PO + 3H_2{}^{18}O \longrightarrow H_3PO_4 + 3CH_3{}^{18}OH$$

The ability of neutral esters of sulphuric acid to react with rupture of the alkyl-oxygen bond is responsible for their alkylating action. For instance, alkyl sulphates are widely used as alkylating agents. The esters of nitric and perchloric acids are not suitable for this purpose because of their explosiveness.

A. Preparation of Esters

1. Esterification reaction:

$$C_2H_5OH + H_2SO_4 \rightleftarrows \begin{matrix} C_2H_5O \\ \\ HO \end{matrix}\!\!\diagdown\!\!\diagup SO_2 + H_2O$$

$$CH_3OH + HNO_3 \rightleftarrows CH_3ONO_2 + H_2O$$

Since the esterification is a reversible reaction, one of the reaction products (or both) has to be removed from the reaction medium. This is achieved either by distillation of the water or ester (if this is a low-boiling compound) or by binding the water.

Hydrogen ions speed up the establishment of equilibrium (i.e., they have a catalytic action on the forward and reverse reactions). Therefore, when alcohols are esterified with weak acids, it is necessary to add a small amount of a strong acid, say, sulphuric acid. Primary alcohols are esterified more readily than secondary ones, and tertiary alcohols undergo esterification the most difficultly. These studies have been carried out by N. A. Menshutkin and are the first physicochemical kinetic investigations in the field of organic compounds.

2. The action of acid chlorides on alcohols (or alkoxides):

$$CH_3OH + Cl-N=O \longrightarrow CH_3O-N=O + HCl$$
$$3CH_3OH + PCl_3 \longrightarrow (CH_3O)_3P + 3HCl$$
$$4CH_3OH + SiCl_4 \longrightarrow (CH_3O)_4Si + 4HCl$$

In this case, HCl is removed by adding ammonia or an organic amine.

It should be recalled that some acid halides react with alcohols in a different manner—with the formation of alkyl halides and not of esters:

$$3CH_3OH + PBr_3 \longrightarrow 3CH_3Br + P(OH)_3$$
$$CH_3OH + PCl_5 \longrightarrow CH_3Cl + POCl_3 + HCl$$
$$3CH_3OH + POCl_3 \longrightarrow 3CH_3Cl + H_3PO_4$$

3. The alkylation effected by the action of alkyl halides on the salts (silver or sodium) of certain acids. This method is more suitable for preparing esters of relatively weak acids, i.e., acids whose anions readily form non-ionic bonds:

$$2CH_3I + Ag_2CO_3 \longrightarrow (CH_3O)_2CO + 2AgI$$

Esters of Boric Acid. The esters of boric acid—trialkyl borates—are readily produced by heating an alcohol and boric acid with addition of concentrated sulphuric acid. Methyl borate (trimethyl borate) boils at 65°C and ethyl borate (triethyl borate) boils at 119°C. Esters of boric acid are readily hydrolysed with water.

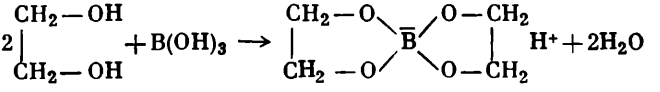
As an element of Group III of the Periodic System, boron has three valency electrons. In boric esters, boron is attached to three oxygen atoms, each of which has supplied one more electron for bond formation; thus, boron has a sextet of electrons and it now lacks a pair of electrons to acquire a stable group of electrons (an octet). Because of this, the molecule of a boric ester is capable of

adding on the alkoxide anion of an alkoxide with the formation of a salt-like compound:

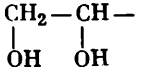
$$(RO)_3B + RONa \longrightarrow (RO)_4B^-Na^+$$

The alkoxide ion RO^- donates two electrons to boron, supplementing its electron shell to an octet and thereby imparting a negative charge to it.

Interacting with boric acid in the cold without addition of sulphuric acid, glycols are esterified at the three hydroxyls of two molecules, and the fourth alcoholic hydroxyl group adds on in the same way as does the alkoxide ion; as a consequence, boron acquires a negative charge, and the hydrogen of the fourth hydroxyl group becomes ionized, and such an ester functions as a strong acid:



Such behaviour is shown by glycerol and all polyhydric alcohols in which the units



rotate freely about the C—C axis.

For polyhydric alcohols with a fixed position of hydroxyl groups, the formation of a strong acid at the expense of the fourth hydroxyl group is possible only if the hydroxyls of a polyhydric alcohol are oriented in one direction and lie in a single plane. The reaction with boric acid is used to establish the configuration of polyhydric alcohols and has been repeatedly employed for this purpose in investigations of sugars.

Esters of Orthosilicic Acid. These esters are prepared by the reaction between silicon tetrachloride and alkoxides or alcohols in the presence of nitrogen bases:

$$SiCl_4 + 4CH_3ONa \rightarrow Si(OCH_3)_4 + 4NaCl$$

Orthosilicic esters are liquids. Methyl orthosilicate boils at 122°C, and the boiling point of ethyl orthosilicate is 156°C. The hydrolysis with water occurs readily even in the cold, but it progresses slowly and, if the amount of water is insufficient, leads to the formation of high-molecular-weight anhydride forms in which the silicon atoms

are joined together through an oxygen atom (**siloxane** groupings):

$$n\mathrm{Si(OCH_3)_4} + (n-1)\,\mathrm{H_2O} \rightarrow$$

$$\rightarrow \mathrm{CH_3O}-\underset{\mathrm{OCH_3}}{\overset{\mathrm{OCH_3}}{\mathrm{Si}}}-\left(-\mathrm{O}-\underset{\mathrm{OCH_3}}{\overset{\mathrm{OCH_3}}{\mathrm{Si}}}-\right)_{n-2}-\mathrm{O}-\underset{\mathrm{OCH_3}}{\overset{\mathrm{OCH_3}}{\mathrm{Si}}}-\mathrm{OCH_3} + (2n-2)\mathrm{CH_3OH}$$

These high-molecular-weight compounds known as **polyalkoxysiloxanes** or **silicones** find use as binders capable of withstanding rather high temperatures, say, for coating moulds used for precise casting of metals.

Dialkyldichlorosilanes react like $SiCl_4$. For example, $(CH_3)_2SiCl_2$ forms dialkoxyl derivatives:

$$(\mathrm{CH_3})_2\mathrm{SiCl_2} + 2\mathrm{CH_3OH} \rightarrow (\mathrm{CH_3})_2\mathrm{Si(OCH_3)_2} + 2\mathrm{HCl}$$

Their hydrolysis yields, with a deficiency of water, so-called **polyalkylsiloxanes**:

$$n(\mathrm{CH_3})_2\mathrm{Si(OCH_3)_2} + (n-1)\mathrm{H_2O} \rightarrow$$

$$\rightarrow \mathrm{CH_3O}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\left(-\mathrm{O}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\right)_{n-2}-\mathrm{O}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{OCH_3} + (2n-2)\mathrm{CH_3OH}$$

They have different (but very high) molecular weights and are viscous liquids used as heat-resistant lubricants, and with still longer siloxane skeletons they are heat resistant, electrically insulating resins and rubbers. (These compounds will be considered in detail in Volume IV under "Organoelement Compounds".)

Esters of Orthotitanic Acid. These esters are obtained, like orthosilicic esters, by the reaction

$$\mathrm{TiCl_4} + 4\mathrm{CH_3OH} + 4\mathrm{NH_3} \rightarrow \mathrm{Ti(OCH_3)_4} + 4\mathrm{NH_4Cl}$$

These liquids, which are readily hydrolysed to methanol and TiO_2, are used for impregnating fabrics to make them waterproof.

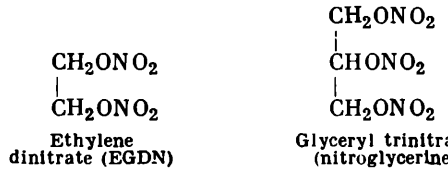
Esters of Nitrous Acid. Nitrites are usually prepared through the action of N_2O_3 on an alcohol or by the dropwise addition of sulphuric acid to sodium nitrite which has been previously mixed with the alcohol. Methyl nitrite, CH_3ONO, is a gas, and ethyl nitrite, C_2H_5ONO, is a liquid which boils at 17°C. Of the esters of nitrous acid only the isoamyl ester

$$\mathrm{CH_3}-\underset{\mathrm{CH_3}}{\mathrm{CH}}-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{ONO}$$

usually known as **amyl nitrite** is especially frequently used since it is more convenient to handle (it boils at 99°C). Amyl nitrite serves as a convenient source of nitrous acid which can be obtained from it by the action of acids directly in the reaction medium. It is used in those cases when a homogeneous reaction medium is required (sodium nitrite is another usual source of nitrous acid but it is insoluble in organic solvents).

The esters of nitrous acid are very toxic; they cause a decrease in blood pressure and relax the contractile muscles.

Esters of Nitric Acid. These esters are produced by the action of a mixture of nitric acid and concentrated sulphuric acid on alcohols. Methyl nitrate, CH_3ONO_2 (b.p. 60°C), and ethyl nitrate, $C_2H_5ONO_2$ (b.p. 87°C), can be distilled off under carefully controlled conditions, but they explode when heated above their boiling points or on being struck or detonated:



Ethylene dinitrate (EGDN) — Glyceryl trinitrate (nitroglycerine)

The nitrates of ethylene glycol and glycerine, which are incorrectly named nitroglycol and nitroglycerine, are used as explosives. **Nitroglycerine** in the pure state (a heavy liquid) is very inconvenient and dangerous to handle. But when it is mixed with an inert material such as diatomaceous earth (kieselguhr; porous SiO_2), the resulting plastic mass, known as **dynamite,** is relatively safe to handle as an explosive. The mixture can still be detonated by use of a small explosive charge attached immediately before use. There also exist other types of dynamite, containing an indifferent material; for example, blasting gelatin—nitroglycerine gelatinized by addition of 10 per cent of cellulose nitrate (nitrocellulose). To some types of smokeless powders prepared from cellulose trinitrate there is added 20-30 per cent of nitroglycerine. Nitroglycerine freezes at a rather high temperature (+11°C) and thus becomes less sensitive to mechanical shock. Glycol nitrate is used to prepare dynamites with a low freezing point (—23°C); in other respects it is similar to glyceryl trinitrate.

Penthrite—pentaerythritol tetranitrate (PETN), $C(CH_2ONO_2)_4$, which is produced by treatment of pentaerythritol with a mixture of nitric and sulphuric acids—is also a high explosive.

The nitric acid esters of glycerol and pentaerythritol have the property of expanding the blood vessels and are used in the treatment of *angina pectoris.*

The esters of nitric acid are but very slowly hydrolysed by water but in the presence of acids or alkalis they are hydrolysed rather rapidly. They also decompose under the action of a solution of Na_2S, the nitrate group being reduced and split off from the alcohol in the form of hydroxylamine.

Esters of Phosphorous and Phosphoric Acids. The esters of phosphorous acid (phosphites) are prepared by the action of phosphorus trichloride on metal alkoxides:

$$3RONa + PCl_3 \rightarrow (RO)_3P + 3NaCl$$

On oxidation they change into esters of phosphoric acid (phosphates):

$$(RO)_3P \xrightarrow{O} (RO)_3PO$$

Phosphites are capable of forming complex compounds with cuprous chloride: $(RO)_3P \cdot CuCl$. When acted on by an alkyl halide they undergo a reaction known as the **Arbuzov rearrangement,** which results in the formation of an ester of alkylphosphonic acid:

$$(CH_3O)_3P + CH_3I \rightarrow \left[\begin{array}{l} CH_3-O \quad CH_3 \\ CH_3-O-P \\ CH_3-O \quad I \end{array}\right] \rightarrow \begin{array}{l} CH_3-O \\ CH_3-O-P-CH_3 + CH_3I \\ \quad\quad O \end{array}$$

Since the rearrangement results in the liberation of alkyl iodide, even a small amount of it is sufficient for any quantity of trialkyl phosphite to be converted into the ester of alkylphosphonic acid.

Methylphosphonic acid may be regarded as a phosphoric acid in which one hydroxyl group has been replaced by a methyl group.

Orthophosphoric acid yields three series of esters—neutral esters and two series of acid esters. The phosphates can be produced by the esterification of alcohols. More often, however, they are made by the action of phosphorus oxychloride on alkoxides:

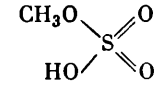
$$3RONa + POCl_3 \rightarrow (RO)_3P=O + 3NaCl$$

Esters of phosphoric acid are high-boiling liquids which are very slowly hydrolysed by water, more rapidly by alkalis and dilute acids. The esters formed by the esterification of higher alcohols (and phenols) are used as plasticizers for plastics and also for extraction of uranyl salts from aqueous solutions.

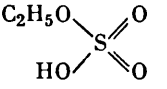
Esters of Sulphurous Acid. Esters of the type $(RO)_2S=O$ are known, but they have found no practical application. The action of thionyl chloride, $SOCl_2$, on alcohols gives rise to an ester which is also an acid chloride and decomposes according to the following scheme:

$$RO-S(=O)-Cl \rightarrow RCl + SO_2$$

Esters of Sulphuric Acid. These esters are made through the reaction of a primary alcohol with concentrated sulphuric acid. An acid ester is formed first, which is known as an **alkylsulphuric acid.** Examples are:



Methylsulphuric acid



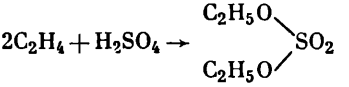
Ethylsulphuric acid

These are strong acids, whose barium and calcium salts are soluble in water, in contrast to the sulphates of barium and calcium. Because of this, it is easy to separate them from excess sulphuric acid.

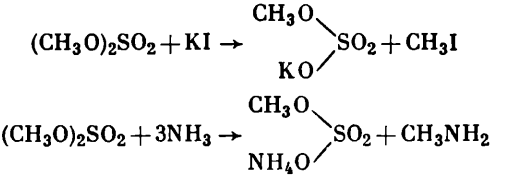
When fuming sulphuric acid is reacted with an excess of an alcohol, neutral esters (sulphates) are obtained:

$$2ROH + 2SO_3 \rightarrow (RO)_2SO_2 + H_2SO_4$$

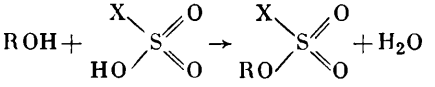
Dimethyl sulphate and diethyl sulphate which are prepared from methanol and ethanol, respectively, have found industrial use as alkylating agents. **Dimethyl sulphate** is an oily heavy liquid boiling at 188°C and is very poisonous. Diethyl sulphate (b.p. 208°C) is more frequently made by leading an excess of ethylene into concentrated sulphuric acid:



On alkylation with dialkyl sulphates use is made of only one alkyl group:



Esters of Chloro- and Fluorosulphonic Acids. These esters are produced by the esterification of alcohols with chlorosulphonic and fluorosulphonic acids, which are the acid halides of sulphuric acid (sulphuryl halides):



Methyl fluorosulphonate is a powerful poison.

Esters of Hypochlorous and Perchloric Acids. The esters of hypochlorous acid are produced by the action of chlorine in the dark on an alcoholic solution of alkali. Methyl hypochlorite, CH_3OCl, boils at 12°C, and ethyl hypochlorite boils at 36°C. These esters are unstable and highly explosive. They are powerful oxidizing agents.

The esters of perchloric acid have been studied little because they readily explode.

Esters of the Oxyacids of Vanadium, Chromium and Other Elements. Examples are $(RO)_3VO$ and $(RO)_2CrO_2$. For acids that are strong oxidizing agents, say, for chromic acid, we know mainly the esters of tertiary alcohols since primary and secondary alcohols are oxidized under the action of these acids to the corresponding aldehydes and ketones.

2.5. Ethers

Substitution of the hydroxyl hydrogens of alcohols by hydrocarbon groups give compounds known as ethers, which may thus be considered to be anhydrides of alcohols. According to whether the alkyl radicals united to the oxygen atom are similar (the same as in the alcohol; ROR) or dissimilar (ROR'), the compounds are known as **simple** or **mixed ethers**. Ethers of both types can be produced by the Williamson method, through the alkylation of sodium alkoxide by an alkyl halide:

$$RONa + R'Cl \rightarrow ROR' + NaCl$$

The most important ether is **diethyl ether** (or, simply, **ether**) $C_2H_5OC_2H_5$, which has been known since the time of alchemists as *sulphuric ether*. It is prepared by the reaction of ethanol with sulphuric acid. First, ethanol is acted on by an excess of sulphuric acid, and then the resulting ethylsulphuric acid is heated up to 140°C, a new portion of the alcohol is added and the ether is distilled off from

the reaction mixture:

$$C_2H_5OH + H_2SO_4 \rightarrow \underset{HO}{\overset{C_2H_5O}{\diagdown\!\diagup}}SO_2 + H_2O$$

Ethylsulphuric acid

$$\underset{HO}{\overset{C_2H_5O}{\diagdown\!\diagup}}SO_2 + C_2H_5OH \rightarrow C_2H_5-O-C_2H_5 + H_2SO_4$$

Diethyl ether (simple ether)

This course of the reaction was also explained by Williamson. Adding another alcohol at the second stage of the reaction, he obtained mixed ethers:

$$\underset{HO}{\overset{C_2H_5O}{\diagdown\!\diagup}}SO_2 + CH_3OH \rightarrow C_2H_5-O-CH_3 + H_2SO_4$$

Methyl ethyl ether (mixed ether)

If ethanol is passed over aluminium oxide (a dehydrating catalyst) heated to 375°C, ethylene and water are formed, but at 300°C the dehydration over Al_2O_3 leads to an ether:

$$2C_2H_5OH \xrightarrow{Al_2O_3;\ 300°C} C_2H_5-O-C_2H_5 + H_2O$$

Another method of synthesizing ethers is the catalytically accelerated addition of alcohols to olefins. As an illustration, diisopropyl ether is produced industrially by adding *sec*-propyl alcohol to propylene in the presence of boron trifluoride:

$$(CH_3)_2CHOH + CH_3-CH=CH_2 \xrightarrow{BF_3} \underset{CH_3}{\overset{CH_3}{\diagdown\!\diagup}}CH-O-CH\underset{CH_3}{\overset{CH_3}{\diagdown\!\diagup}}$$

The physical properties of ethers are given in Table 2.9.

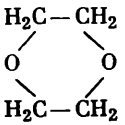
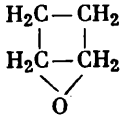
Despite their high molecular weights, ethers boil at much lower temperatures than the corresponding alcohols:

Methyl	°C	Ethyl	°C
ether	−23.7	ether	+34.6
alcohol	+65	alcohol	+78.3

This may be accounted for by the fact that, as a result of the loss of the alcoholic hydroxyl hydrogen, the molecules of an ether are not capable of forming hydrogen bonds and of association (the hydrogen atoms attached to a carbon atom do not, as a rule, form hydrogen bonds) and are therefore ordinary liquids. Indeed, the molecular weights of ethers always correspond to monomeric molecules.

TABLE 2.9. **Ethers**

Formula	Name	Melting point, °C	Boiling point, °C	Density d_4^{20}	Solubility in water, g/100 ml	Dielectric constant at 25°C, ε
CH_3-O-CH_3	Dimethyl ether (methyl ether)	−138.5	−23.7	2.091 (g/l)	3700 (at 18°C)	5.02 (under pressure)
$CH_3CH_2-O-CH_2CH_3$	Diethyl ether (ether)	−116.3 (α-form) −123.3 (β-form)	+34.6	0.714	7.5 (at 20°C)	4.33 (at 20°C)
$CH_3CH_2CH_2-O-CH_2CH_2CH_3$	Di-*n*-propyl ether (propyl ether)	−122	91	0.736	0.25 (at 25°C)	3.39 (at 25.7°C)
$CH_3-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-O-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_3$	Di-*sec*-propyl ether (diisopropyl ether)	−60	67.5	0.726	0.2	3.88
$CH_3CH_2CH_2CH_2-O-CH_2CH_2CH_2CH_3$	Di-*n*-butyl ether (butyl ether)	−95.2	142	0.784 (d_4°)	Difficultly soluble	—
$CH_3-O-CH_2CH_2-OH$	Monomethyl ether of ethylene glycol (methyl cellosolve)	—	124.3	0.9660	∞	—

$C_2H_5-O-CH_2CH_2-OH$	Monoethyl ether of ethylene glycol (ethyl cellosolve)	—	135.1	0.9311	∞	—
$CH_3-O-CH_2CH_2-OCH_3$	Dimethyl ether of ethylene glycol (1,2-dimethoxyethane)	−58	84.5	0.863	∞	—
$C_2H_5-O-CH_2CH_2-OC_2H_5$	Diethyl ether of ethylene glycol (1,2-diethoxyethane)	—	123.5	0.8484	—	—
	1,4-Dioxan	11.7	101.5	1.035	∞	2.21
	Tetrahydrofuran	−65	66	0.889	Readily soluble	—

Diethyl ether is only sparingly soluble in water (6 per cent at 20°C) and is itself a solvent with respect to water (about 1.2 per cent); it is miscible with alcohols, hydrocarbons, and with most organic solvents and immiscible with ethylene glycol and glycerol. Diethyl ether has a considerable solubility in sulphuric acid and in concentrated hydrochloric acid.

The solubility of ethers in protonic acids is due to the basic properties of the ether oxygen. Like the nitrogen in ammonia, the oxygen exhibits basic properties because of the presence of two free electron pairs on it (nitrogen has one free pair of electrons). These electron pairs cannot be made use of for the manifestation of ordinary valency since there are already eight electrons (an octet of electrons) around the oxygen in the ether molecule. The oxygen cannot therefore accept electrons but can alone supply one pair of electrons for bond formation, say, with the hydrogen cation. After the cation has been added the system becomes positively charged:

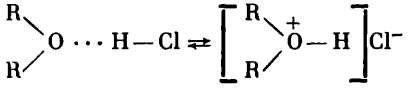
$$(C_2H_5)_2\ddot{O} + H^+ \rightarrow [(C_2H_5)_2OH]^+$$

and the next electron pair cannot be supplied to a new cation.

The basicity of ether, like that of other weak bases, can be characterized by the magnitude of the equilibrium constant K_a (for more detail, see page 201) of the reaction:

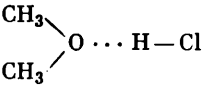
$$[(C_2H_5)_2OH]^+ \rightleftarrows (C_2H_5)_2O + H^+$$

For diethyl ether $pK_a = -3.6$ (pK_a is the common logarithm of K_a taken with the opposite sign). Since water is a base comparable with ether in strength (for water $pK_a = -3.42$), ether is displaced from solutions in acids by water into the upper supernatant layer. As shown by measurements, the electrical conductivity of solutions of hydrogen chloride in dry ether is very low. This means that the labile compounds of the ether with an acid are but very insignificantly similar in character to oxonium compounds and are evidently formed largely with the aid of a hydrogen bond:



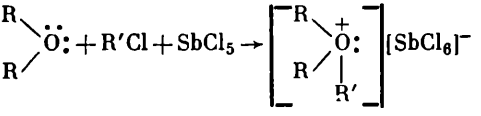
When gaseous dimethyl ether reacts with gaseous HCl (in the gas and not in the liquid phase), a so-called Friedel compound is formed, which has the composition $(CH_3)_2O \cdot HCl$ and is a gas, like the starting ether, though a higher-boiling one. It cannot be salt-like, otherwise it would be solid. Indeed, the physical studies of the

Friedel compound have shown the presence of a hydrogen bond in it (Ya. K. Syrkin):



Ethers form complex compounds with many salts, for example, $R_2O \cdot MgCl_2$, $R_2O \cdot HgBr_2$, $(R_2O)_2 \cdot SnCl_4$. A very stable liquid compound is formed by ethers and boron trifluoride ($R_2O \cdot BF_3$).

The free pair of electrons on the ether oxygen atom can also be supplied to the alkyl cation, say, according to the following reaction (Meerwein):

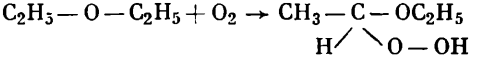


(see Sec. 2.6).

In contrast to esters, ethers are hydrolysed neither by aqueous solutions of alkalis nor by dilute acids. Strong hydriodic acid decomposes ethers:

$$ROR + HI \rightarrow RI + ROH$$

When diethyl ether is allowed to stand in contact with air for some time, it is slowly oxidized and is then found to contain explosive hydroperoxides:



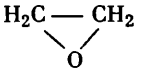
The formation of peroxide compounds has been the cause of numerous accidents during the distillation of ethers. It is for this reason that ether which has been standing in contact with air for some time must be tested for peroxides by the reaction with KI in the presence of starch. If the reaction is positive (oxidation of KI to iodine), the peroxides must be removed by their reduction (for example, with ferrous salts) and by washing the ether with water.

Diethyl ether is extensively used in the laboratory as an ordinary solvent, for extractions from aqueous solutions, and also as a medium for preparation of organomagnesium compounds. In industry, its use is rather limited because it is highly inflammable and its vapour forms an explosive mixture with air. In medicine it finds use as an anesthetic in surgical operations.

Diisopropyl ether is an excellent antiknock additive to motor fuels. Dibutyl ether is used as a solvent.

A. Ethers of Polyhydric Alcohols

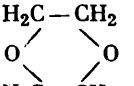
If ethers are regarded as the products of dehydration of alcohols, then for ethylene glycol the following ethers may be expected to form at the expense of one or more molecules of ethylene glycol:



Ethylene oxide

$HOCH_2CH_2-O-CH_2CH_2OH$

Diethylene glycol



Dioxan

$$HOCH_2CH_2-(OCH_2CH_2)_n-OCH_2CH_2OH$$

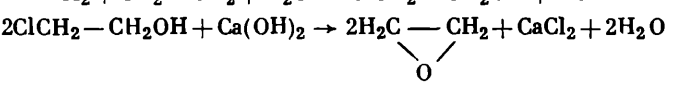
Polyethylene glycol

It is only dioxan that can be obtained directly by dehydration of ethylene glycol by sulphuric acid (A. E. Favorsky). All other ethers, like the mixed ethers of ethylene glycol ($RO-CH_2-CH_2-OH$), are produced from ethylene oxide. It is for this reason that we begin our study with ethylene oxide.

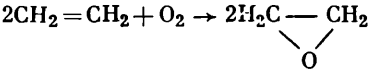
Ethylene oxide is manufactured on a large industrial scale from ethylene by either of the following two ways:

1. Via ethylene chlorohydrin by a series of reactions already familiar to us:

$$Cl_2 + CH_2=CH_2 + H_2O \rightarrow ClCH_2-CH_2OH + HCl$$

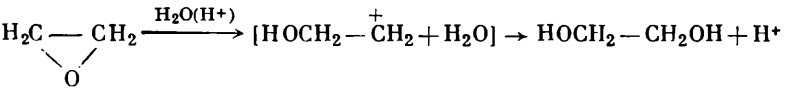


2. By direct oxidation of ethylene with atmospheric oxygen at about 250°C over a catalyst consisting of metallic silver promoted with a small amount of AgCl:

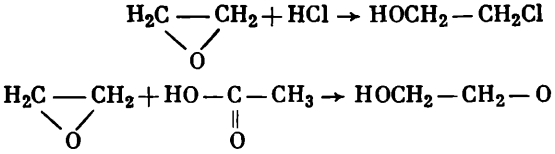


Ethylene oxide boils at 10.7°C. In its chemical properties, ethylene oxide bears little resemblance to ethers. It is a very reactive substance; its reactions are accompanied by the opening of the three-membered ring when the oxygen atom is attacked by a hydrogen ion.

For example, in aqueous solutions of acids the ring of ethylene oxide is ruptured and ethylene glycol is formed:



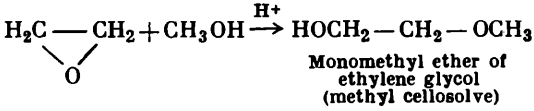
In anhydrous acids, the attack beginning in the same way ends with addition of the acid anion and formation of chlorohydrin (reaction 1) or of half-esters of ethylene glycol (reaction 2):



(1)

(2)

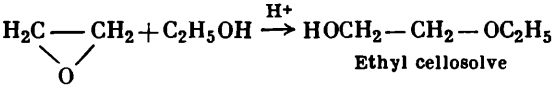
If the acid treatment is carried out in an alcoholic solution, mixed ethers of ethylene glycol (called cellosolves) are obtained:



Monomethyl ether of ethylene glycol (methyl cellosolve)

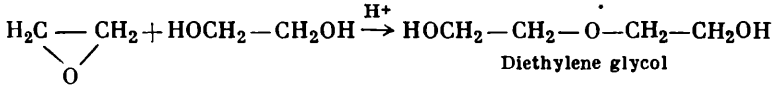
Additional methylation of the monomethyl ether, say, with the aid of dimethyl sulphate, gives a dimethyl ether of ethylene glycol—**monoglyme** which finds an ever increasing use as a laboratory solvent, for example, in the synthesis of organometallic compounds.

In the presence of ethanol, a monoethyl ether is formed:



Ethyl cellosolve

Ethylene glycol itself may be used as an alcohol:



Diethylene glycol

The dimethyl ether of diethylene glycol is known as **diglyme** and is also employed as a solvent.

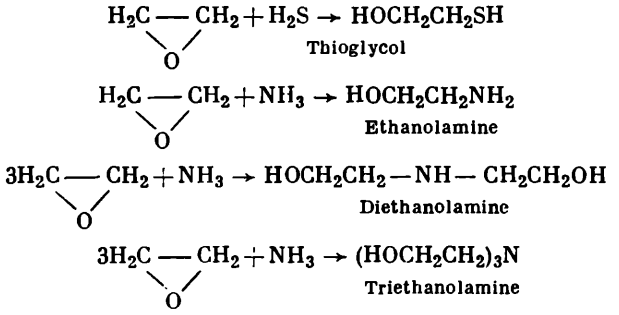
Since the reaction product is an alcohol too, polyethylene glycols are also formed if an excess of ethylene oxide is present.

The alkylation of diethylene glycol with an alcohol yields so-called **carbitols** of the general formula $ROCH_2CH_2—O—CH_2CH_2OH$.

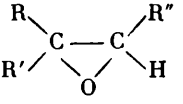
Cellosolves and carbitols are manufactured on an industrial scale and are utilized as solvents which have the properties both of alco-

hols and ethers, for example, in the paint and varnish industry and, in general, for dissolution of cellulose esters.

The ring of ethylene oxide can also be ruptured by hydrogen sulphide and ammonia:

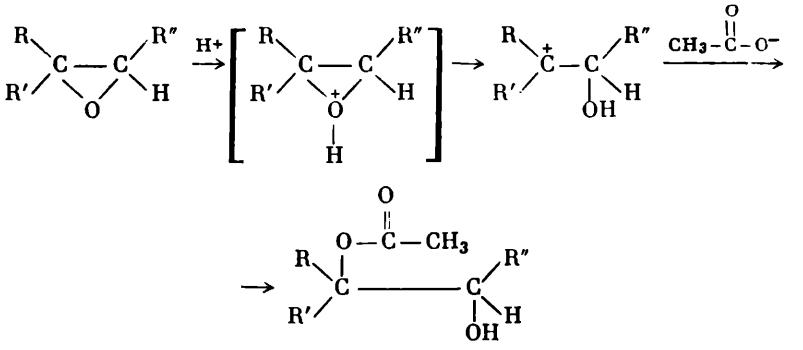


Oxides of the type



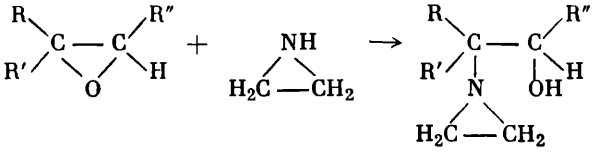
(where R, R′, R″ = alkyl or H)

are ruptured, if these reactions are carried out in acid medium, in such a manner that the hydroxyl turns out to be attached to the carbon which carries the largest number of hydrogen atoms, i.e., a primary $-CH_2OH$ group is predominantly formed, and if this is impossible, the secondary group $-RCHOH$ predominates (A. K. Krasusky). This is accounted for by the fact that the transiently formed carbonium ion is the most stable when the positive charge is carried by the tertiary carbon atom, and the least stable when the positive charge is on the primary carbon atom (see Volume IV, "Carbonium Ions"):



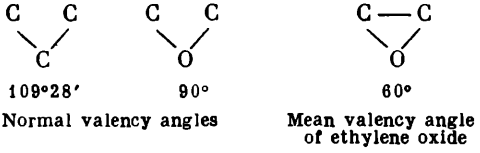
where R, R′, R″ = alkyl or H.

Such a ring disclosure, particularly when caused by the action of ethyleneimine (the nitrogen analogue of ethylene oxide) has been thoroughly studied by I. A. Dyakonov who verified the regularity established by A. K. Krasusky:



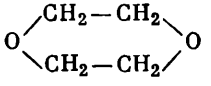
Many of the reactions based on the scission of the ring of ethylene oxide are used in industrial syntheses.

The instability inherent in ethylene oxide is typical of three-membered rings and, in general, of those compounds in which the angles of valency bonds differ sharply from normal angles:

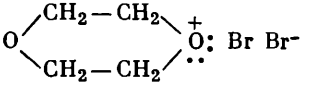


The thermal instability of ethylene oxide is exhibited on its isomerization at 400°C to acetaldehyde (one of the industrial methods of synthesizing acetaldehyde). A drop of strong sulphuric acid dimerizes ethylene oxide to dioxan.

Cyclic ethers with normal valency angles do not differ in stability from ethers with an open chain. For example, *dioxan*

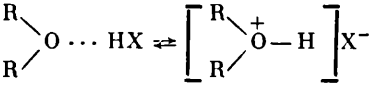


obtained by heating ethylene glycol with sulphuric acid (A. E. Favorsky) is quite stable. Dioxan is a liquid which boils at 101.5°C and is miscible with water in all proportions; it is an excellent solvent but its use as such in industrial practice is hindered by its slight toxicity. The basic properties of dioxan are more prominent than those of diethyl ether (pK_a for the protonated form of dioxan is 3.2). Dioxan forms numerous complexes with salts of heavy metals. With bromine it gives a solid dibromide of the following structure:

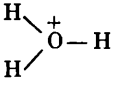


2.6. Oxonium Compounds

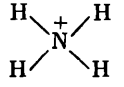
As has already been mentioned, ethers are converted by strong acids to unstable compounds linked by hydrogen bonding, which partly exist in oxonium form. These are secondary oxonium compounds:



The simplest inorganic oxonium compound is the hydrated hydrogen ion—the hydroxonium ion (or the hydronium ion), which is a slightly stable analogue of the more stable ammonium ion:

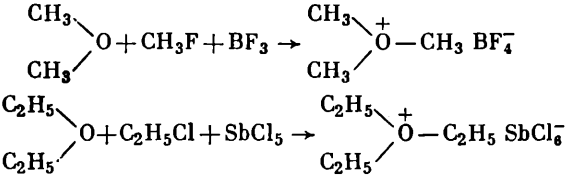


Hydronium ion

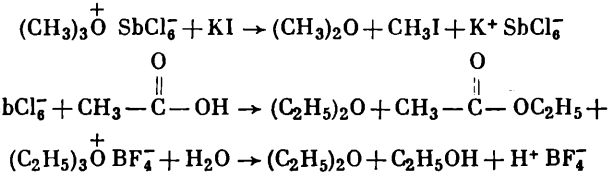


Ammonium ion

In 1928 Meerwein discovered tertiary oxonium salts which can be prepared from ethers by the following reactions:



The role of the halides BF_3 and $SbCl_5$ consists in the heterolytic splitting of the halogen of an alkyl halide and in binding it into an exceptionally stable anion. Trialkyloxonium compounds with complex anions are solid, quite stable salt-like compounds. When an attempt is made to replace the anion in these salts by the anion of any ordinary acid, i.e., on interaction with acids or their salts or even with water, oxonium salts decompose to yield an ether and an alkylated anion:

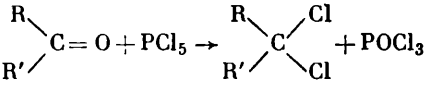


Trialkyloxonium salts are the strongest alkylating agents among those already considered (stronger than alkyl halides and dialkyl sulphates).

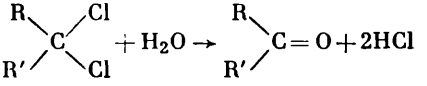
2.7. Carbonyl Compounds (Aldehydes and Ketones)

The next important class of the oxygen derivatives of alkanes consists of carbonyl compounds. As follows from their reactions and methods of preparation, carbonyl compounds may be considered to be alkanes in which two hydrogen atoms at one carbon atom have been replaced by a divalent oxygen atom. Thus, the functional group of carbonyl compounds is the *carbonyl group* >C=O. The presence of a carbonyl group in carbonyl compounds can be confirmed by the following reactions.

The oxygen atom of the carbonyl group can be replaced, through the action of phosphorus pentachloride, by two chlorine atoms to give a dichloroalkane:



That the structure of the carbon chain undergoes no change in this reaction follows from the fact that the hydrolysis of the dichloroalkane formed gives the same carbonyl compound:



Using this reaction, Butlerov carried out the hydrolysis of methylene iodide, CH_2I_2, and synthesized the simplest carbonyl-containing compound—formaldehyde (methanal), HCHO.

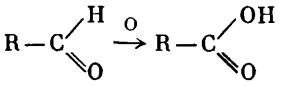
Thus, it has been proved that the oxygen atom is attached, through both valency bonds, to the same carbon atom. The presence of the carbon-oxygen double bond, C=O, in carbonyl compounds has also been corroborated by numerous addition reactions given below. A no less conclusive evidence of the structure of carbonyl compounds is provided by methods of their synthesis.

Aldehydes and **ketones** are two important classes of carbonyl-containing compounds*, whose reactions have much in common but there are significant differences too. The nomenclature of the two classes of compounds is different.

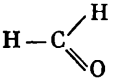
The trivial or common names of aldehydes are derived from the names of the corresponding carboxylic acids into which they are

* The carbonyl group occurs in carboxylic acids and their derivatives also but in the aldehydes and ketones, the carbon of the carbonyl group is joined either to two other carbon atoms (in ketones) or to a carbon and hydrogen atom (in aldehydes).— *Tr.*

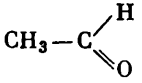
converted on oxidation:



The ending *-ic* (or *-oic*) in the name of the acid is replaced by the word *aldehyde*. Thus, the first member of the series

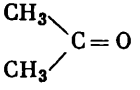


is called formaldehyde and the second member

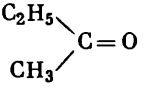


is known as acetaldehyde, etc.

Ketones are named according to the two groups attached to the carbonyl group, the word ketone being preceded by separate words specifying the radicals. For example,



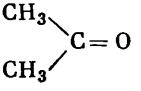
Dimethyl ketone



Methyl ethyl ketone

Ketones with identical radicals are sometimes given the Latin names of the acids, from the calcium salts of which they can be made by dry distillation (see methods of preparation); for example, acetone from acetate, butyrone from butyrate, stearone from stearate.

According to the Geneva nomenclature, the names of aldehydes (alkanals) are derived from the names of the hydrocarbons with the same number of carbon atoms by adding the ending *—al*: methanal, ethanal, etc. For ketones (alkanones) the Geneva nomenclature recommends the ending *-one*: propanone, butanone, etc. As is always the case, the position of the functional group in the chain is designated by a numeral. From the structure of the simplest representative of ketones



it follows that a ketone cannot have less than three carbon atoms.

The names and some of the physical properties of aldehydes and ketones are given in Tables 2.10 and 2.11.

In contrast to alcohols which are liable to association, aldehydes and ketones are unassociated liquids. Therefore they boil at a much

TABLE 2.10. Aldehydes

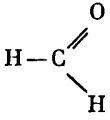
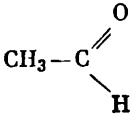
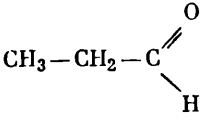
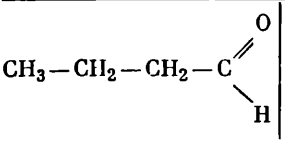
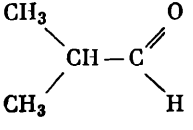
Formula	Name		Melting point, °C	Boiling point, °C	Density d_4^{20}	Dipole moment in benzene at 20°C, D
	trivial	Geneva				
	Formaldehyde	Methanal	—92	—21.0	0.815 (d_4^{-20})	2.27 (gas at 147-247°C)
	Acetaldehyde	Ethanal	—123.5	+21.0	0.780	2.49
	Propionaldehyde	Propanal	—81	48.8	0.807	2.54
	Butyraldehyde	Butanal	—99.0	75.7	0.817	2.57
	Isobutyraldehyde	2-Methylpropanal	—65.9	63.5	0.794	2.58

TABLE 2.10. (continuation)

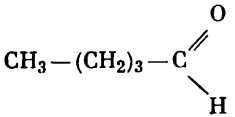
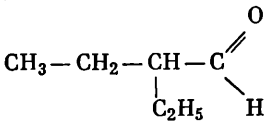
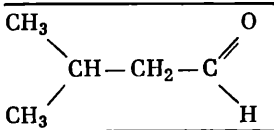
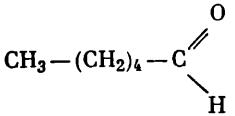
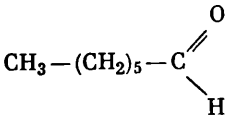
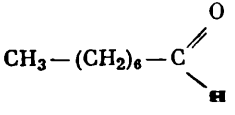
Formula	Name		Melting point, °C	Boiling point, °C	Density d_4^{20}	Dipole moment in benzene at 20°C, D
	trivial	Geneva				
	Valeraldehyde	Pentanal	—91.5	103.4	0.809	2.57
	α-Ethylbutyraldehyde	3-Ethylbutanal	—	117	0.814	—
	Isovaleraldehyde	2-Methylbutanal	—51	92.5	0.803 (d_4^{17})	2.60
	Caproaldehyde	Hexanal	—56	131	0.833	—
	Enanthaldehyde or oenanthal	Heptanal	—45	155	0.850	2.56 (at 22°C)
	Caprylaldehyde	Octanal	—	163.4, 171.0	0.821	—

TABLE 2.11. **Ketones**

Formula	Name		Melting point, °C	Boiling point, °C	Density d_4^{20}	Dipole moment in benzene at 15°C, D
	trivial	Geneva				
$CH_3-C(=O)-CH_3$	Acetone	2-Propanone	—95.0	56.5	0.792	2.72 (at 18°C)
$CH_3-C(=O)-C_2H_5$	Methyl ethyl ketone	2-Butanone	—86.4	79.6	0.805	2.79
$CH_3-C(=O)-C_3H_7$-*n*	Methyl *n*-propyl ketone	2-Pentanone	—77.8	101.7	0.809	2.72
$C_2H_5-C(=O)-C_2H_5$	Diethyl ketone	3-Pentanone	—42.0	102.7	0.816 (d_4^{19})	2.72
$CH_3-C(=O)-CH(CH_3)_2$	Methyl isopropyl ketone	3-Methyl-2-butanone	—92	93.0	0.815 (d_4^{15})	2.76 (at 20°C)
n-$C_3H_7-C(=O)-C_3H_7$-*n*	Dipropyl ketone	4-Heptanone	—32.6	144	0.8174	2.73
iso-$C_3H_7-C(=O)-C_3H_7$-*iso*	Diisopropyl ketone	2,4-Dimethyl-3-pentanone	—69.0	123.7	0.8062	2.74 (at 25°C)
$CH_3-C(=O)-C(CH_3)_2-CH_3$	*tert*-Butyl methyl ketone or pinacolone (pinacolin)	3,3-Dimethyl-2-butanone	—52.5	106.2	0.8208 (d_4^0)	2.79

lower temperature than the corresponding alcohols. For example,

	b. p., °C		b. p., °C
$CH_3-CH_2-CH_2OH$	97.2	$CH_3-\underset{\displaystyle OH}{\underset{\vert}{CH}}-CH_3$	82
$CH_3-CH_2-\overset{\displaystyle O}{\overset{\displaystyle \vert\vert}{C}}-H$	49	$CH_3-\overset{\displaystyle O}{\overset{\displaystyle \vert\vert}{C}}-CH_3$	56

Usually ketones boil at a somewhat higher temperature than the isomeric aldehydes:

	b. p., °C		b. p., °C
$CH_3-\overset{\displaystyle O}{\overset{\displaystyle \vert\vert}{C}}-CH_3$	56	$CH_3-\overset{\displaystyle O}{\overset{\displaystyle \vert\vert}{C}}-CH_2-CH_3$	79.6
$CH_3-CH_2-\overset{\displaystyle O}{\overset{\displaystyle \vert\vert}{C}}-H$	49	$CH_3-CH_2-CH_2-\overset{\displaystyle O}{\overset{\displaystyle \vert\vert}{C}}-H$	75.7

Chain branching causes, just as in other series of compounds, a decrease in the boiling point and density. The dipole moment of aldehydes and ketones varies little from compound to compound and amounts to about 2.7×10^{-18} electrostatic units or 2.7 D*. From the constancy of this quantity it follows that 2.7 D is the dipole moment of the carbonyl group (for the dipole moment, see page 425).

As shown by X-ray studies, the C=O distance in the carbonyl group is equal to 1.22 Å. Had the carbonyl group a structure with a semi-polar bond, i.e., $>\overset{+}{C}-\overline{O}$, the dipole moment must have been equal to the product of the charge on the electron, 4.8×10^{-10}, by the distance 1.22×10^{-8} cm, namely, 5.8×10^{-18} electrostatic units (5.8 D), i.e., it would have been twice as that observed (2.7 D). At the same time, the observed dipole moment, 2.7 D, is greater than the doubled dipole moment of the single carbon-oxygen bond, C—O, in esters ($1.2 \times 2 = 2.4$ D). Hence, one of the two bonds in the C=O group is more polarizable than the other (a π-bond and σ-bond, see page 312), which may be depicted schematically by indicating the shift of the π-electron pair of the double bond with the aid of a curved arrow:

$$>\overset{\delta+}{C}=\overset{\delta-}{O}$$

* D is the Debye unit equal to 10^{-18} electrostatic units (esu).

Physically, the polarizability of the π-bond manifests itself in the high molecular refraction* of the aldehydes and ketones.

Most of the chemical properties of aldehydes and ketones are in agreement with the high dipole moment of the carbonyl group, the presence of a partial positive charge on its carbon atom and especially with the further considerable polarizability of the double (>C=O) bond. This is reflected, first, in the ability of aldehydes and ketones to enter readily into addition reactions and, second, in the tendency of the α-hydrogen atoms to ionize, i.e., to leave the molecule as a proton on attack by basic reagents. The α-hydrogen atoms are those attached to the carbon atom adjacent to the carbonyl group.

A. Synthesis of Aldehydes and Ketones

1. **Preparation from alcohols.** From the structural similarity between aldehydes and primary alcohols and between ketones and secondary alcohols it follows that it is possible to prepare the primary and secondary alcohols from aldehydes and ketones, respectively (see pages 127 and 133) and aldehydes and ketones from the alcohols by catalytic dehydrogenation or oxidation.

The catalytic dehydrogenation of alcohols is carried out by passing the alcohol vapour over finely divided copper. This involves the splitting-off of a hydrogen molecule:

$$R-CH_2OH \xrightarrow{Cu} R-C\begin{matrix}H\\ \diagup\\ \diagdown\\ O\end{matrix} + H_2$$

$$R-\underset{\displaystyle OH}{\underset{|}{CH}}-R' \xrightarrow{Cu} R-\overset{\displaystyle O}{\overset{\|}{C}}-R' + H_2$$

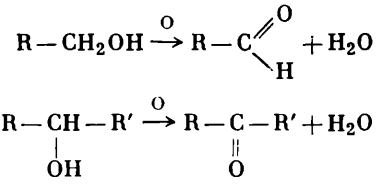
The oxidation of alcohols can be effected catalytically—by atmospheric oxygen over the same copper catalyst. This method is used on an industrial scale to produce large amounts of formaldehyde from methanol:

$$2H-\underset{\displaystyle H}{\overset{H}{\overset{|}{\underset{|}{C}}}}-O-H + O_2 \xrightarrow{Cu} 2\begin{matrix}H\\ \diagdown\\ \diagup\\ H\end{matrix}C=O + 2H_2O$$

The oxidation can also be carried out by the wet method, using an oxidizing agent such as potassium dichromate mixed with sul-

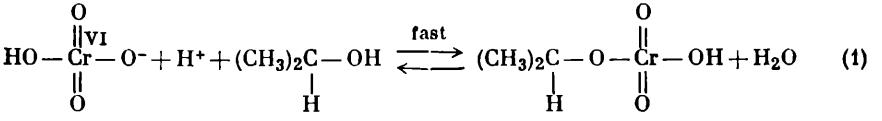
* For molecular refraction, see page 441.

phuric acid ($K_2Cr_2O_7 + H_2SO_4$):

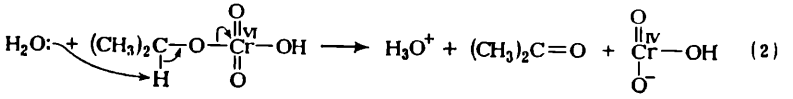


The long-known reaction of oxidation of alcohols by chromic acid has been thoroughly studied by F. H. Westheimer using secondary propyl alcohol.

Within the range of moderate concentrations of the acid the rate of the reaction is proportional to the concentration of $HCrO_4^-$ and to the square of the hydrogen ion concentration. This is in agreement with the assumption that $HCrO_4^-$ is first converted into undissociated H_2CrO_4, which esterifies the alcohol. The acid ester of the alcohol and chromic acid undergoes (in the presence of water as a proton-acceptor) an internal oxidation-reduction reaction shown in the scheme below by curved arrows which indicate the transfers of electron pairs*, as a result of which a carbonyl compound is formed:



(1)



(2)

That the chain of electron transfers ends at the chromium atom means that chromium(VI), having accepted an electron pair, under-

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* It should be emphasized here that curved arrows are always used to indicate the migration of electron pairs. It is necessary, however, to differentiate between two kinds of electron migration.

1. **Electron shift** is a complete transfer of electrons associated with the heterolytic scission of the existing bonds and formation of new ones, this being exemplified by the representations of reaction mechanisms given above. In this case, a curved arrow is directed from the donor to the acceptor atom, or else indicates the site between two atoms of both reactant molecules where a new bond is formed. Electron shift that occurs inside one molecule is defined as the *tautomeric shift* (*T*).

2. **Mesomeric shift** of electron pairs (always taking place inside a single molecule) is the migration of electron pairs, which does not involve the rupture of the existing bonds and formation of new ones; it stops, so to speak, halfway. The phenomenon of mesomerism and mesomeric shift will be considered on page 235 and, in more detail, on page 318.

goes a change to the tetravalent unstable state, following which Cr^{IV} disproportionates into Cr^{VI} and Cr^{III}. The formation of the esters of chromic acid by the action of alcohols has been proved by their extraction with an organic solvent. The esters are capable of decomposing with the formation of aldehydes and ketones.

A comparison of the rates of oxidation of two alcohols—an ordinary one and the alcohol labelled with deuterium

$$(CH_3)_2C(H)-OH \qquad (CH_3)_2C(D)-OH$$

points to the considerably (by several times) slower oxidation of the deuterated alcohol. Such a high isotope effect is observed for compounds of deuterium when the D—C bond takes a direct part in the reaction, just as in reaction (2). A check of the reaction mechanism by the use of $HCrO_4^-$ with a labelled oxygen is impossible because of the equilibrium

$$2HCrO_4^- \rightleftarrows Cr_2O_7^{2-} + H_2O$$

In the synthesis of aldehydes by the oxidation of alcohols, the aldehyde should be removed immediately from the reaction mixture in order to prevent its oxidation to the corresponding carboxylic acid:

$$R-C(=O)-H + O \longrightarrow R-C(=O)-OH$$

An exceedingly convenient and frequently used laboratory method is the **Oppenauer oxidation** of secondary alcohols with an excess of acetone in the presence of an aluminium alkoxide, a weakly basic catalyst, which accelerates the establishment of equilibrium:

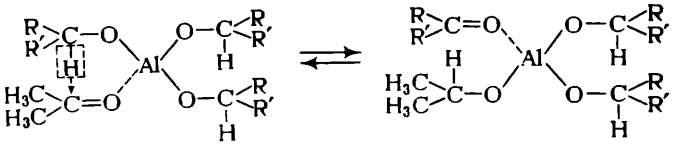
$$R-CH(OH)-R' + CH_3-C(=O)-CH_3 \xrightleftharpoons{[(CH_3)_2CHO]_3Al} R-C(=O)-R' + CH_3-CH(OH)-CH_3$$

The stoichiometric equation of the reaction does not disclose its mechanism which includes **hydride transfer**, i.e., the transfer of the hydrogen atom together with the electron pair from one covalent bond to another.

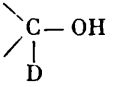
The role of an aluminium alkoxide* consists in the coordination binding of the ketone. Hydride transfer takes place within the coor-

* The frequently used aluminium *tert*-butoxide or isopropoxide when reacted with an excess of the original alcohol gives the corresponding secondary alkoxide.

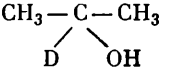
dination compound formed, as a consequence of which an equilibrium sets in:



The hydride transfer has been verified by using a deuterium-labelled secondary alcohol as a starting compound. The deuterium from the grouping



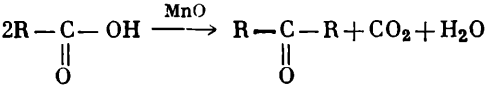
is transferred to acetone and this results in the formation of deuterated isopropyl alcohol



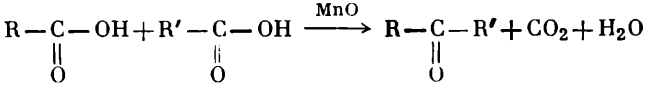
To displace the equilibrium and to convert all the original secondary alcohol into the ketone, the equilibrium mixture containing excess acetone is heated so that the isopropyl alcohol is distilled off together with part of acetone and the original alcohol and the ketone formed are retained in the reaction mixture as less volatile compounds.

The same equilibrium system is used for a reaction which is the reverse of the Oppenauer oxidation of secondary alcohols, i.e., for the reduction of ketones to secondary alcohols (called the Meerwein-Ponndorf reduction). In this case, not the acetone but isopropyl alcohol is taken in excess, and the equilibrium mixture is heated so as to distil off all the acetone formed.

2. **Preparation from acids.** The vapour of the acid is passed at a temperature above 300°C over a catalyst—manganous or thorium oxide:



If two different acids are heated together, there will result a mixture of ketones, including a ketone RCOR′:



If one of the acids taken is formic acid, the principal reaction product is an aldehyde:

$$R-\underset{\underset{O}{\|}}{C}-OH+H-\underset{\underset{O}{\|}}{C}-OH \xrightarrow{MnO} R-\underset{\underset{O}{\|}}{C}-H+CO_2+H_2O$$

This reaction has originated from the old Piria method—the dry distillation of the calcium salt of an acid (or a mixture of acids). In its time the method of dry distillation of calcium acetate was the only industrial method of preparing acetone (hence the name of acetone):

$$(CH_3-\underset{\underset{O}{\|}}{C}-O)_2Ca \rightarrow CH_3-\underset{\underset{O}{\|}}{C}-CH_3+CaCO_3$$

This reaction throws light also on the role of metal oxides as catalysts for the method of preparation of ketones described above.

3. **Syntheses with the aid of Grignard reagents.** When organomagnesium compounds are reacted with the derivatives of formic acid given below, aldehydes are formed (at a low temperature), and when they are acted on by some of the derivatives of other acids, ketones result:

$$RMgBr+H-C\begin{matrix}=O\\ \diagdown ONa\end{matrix} \rightarrow R-C\begin{matrix}=O\\ \diagdown H\end{matrix}+NaBr+MgO$$

Sodium formate

$$RMgBr+H-C\begin{matrix}=O\\ \diagdown OC_2H_5\end{matrix} \rightarrow R-C\begin{matrix}=O\\ \diagdown H\end{matrix}+Mg\begin{matrix}\diagup Br\\ \diagdown OC_2H_5\end{matrix}$$

Ethyl formate (excess)

$$RMgBr+R'-\underset{\underset{O}{\|}}{C}-Cl \rightarrow R-\underset{\underset{O}{\|}}{C}-R'+MgBrCl$$

An acid chloride

$$RMgBr+R'-C\equiv N \rightarrow R-\underset{\underset{NMgBr}{\|}}{C}-R' \xrightarrow{2H_2O} R-\underset{\underset{O}{\|}}{C}-R'+NH_3+Mg\begin{matrix}\diagup Br\\ \diagdown OH\end{matrix}$$

An acid nitrile

4. **Hydration of acetylenes.** Acetylene and its homologues when acted on by water in the presence of catalysts (mercuric salts) are converted into carbonyl compounds. In this reaction, only acetylene forms an aldehyde, namely, acetaldehyde (the **Kucherov reaction**).

This method is one of the principal industrial methods for the preparation of acetaldehyde:

$$H-C\equiv C-H+H_2O \xrightarrow{Hg^{2+}} CH_3-C\begin{matrix}=O\\ \diagdown H\end{matrix}$$

All the homologues of acetylene give ketones in accordance with Markovnikov's rule (see page 336):

$$R-C\equiv C-H+H_2O \xrightarrow{Hg^{2+}} R-\underset{\underset{O}{\|}}{C}-CH_3$$

Acetaldehyde is made from ethylene which is first converted into the oxide and then isomerized (see page 161) or by the action of water on the complex (Schmidt, Ya. K. Syrkin, N. I. Moiseev):

$$Na^+[Cl_3Pd\cdot C_2H_4]^- + H_2O \longrightarrow Pd + 2HCl + NaCl + CH_3-C\begin{matrix}=O\\ \diagdown H\end{matrix}$$

B. Specific Reactions for Synthesis of Aldehydes

1. **Reduction of acid derivatives to aldehydes.** We shall confine ourselves to the consideration of the **Rosenmund reduction**—the catalytic reduction of acid chlorides by hydrogen* (the catalyst is palladium supported on barium sulphate):

$$R-\underset{\underset{O}{\|}}{C}-Cl + H_2 \xrightarrow{Pd} R-\underset{\underset{O}{\|}}{C}-H + HCl$$

This reaction shows the structural relations between aldehydes and acid chlorides.

2. **Oxo synthesis.** In 1938, Reppe discovered an interesting reaction for synthesis of aldehydes from olefins (alkenes) and a mixture of carbon monoxide and hydrogen (the so-called water gas). The reaction (hydroformylation) is carried out at a temperature** slightly higher than 100°C and a pressure of 200 kg/cm^2 in the presence of cobalt as a catalyst. Obviously, the simplest aldehyde that can be prepared by this process (starting with the simplest olefin—ethylene) is propyl aldehyde (or propionaldehyde):

$$CH_2=CH_2+CO+H_2 \xrightarrow{Co} CH_3-CH_2-CH=O$$

The homologues of ethylene give a mixture of straight- and branched-chain aldehydes.

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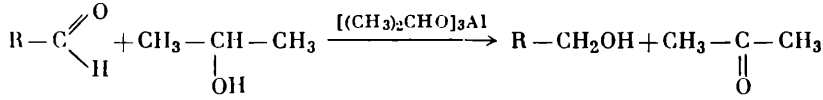
* Also known as the *Rosenmund hydrogenation* of acid chlorides.—*Tr.*

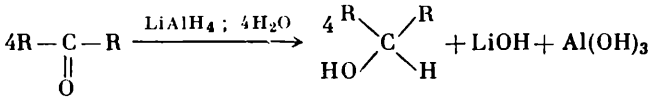
** At higher temperatures the aldehydes formed are reduced to alcohols.

C. Chemical Properties of Aldehydes and Ketones

Addition reactions. 1. *Reduction.* The reduction of aldehydes and ketones to primary and secondary alcohols, respectively, has already been considered in the description of methods of preparing alcohols. Here we shall cite, in addition, only the Meerwein-Ponndorf reduction of aldehydes to primary alcohols by *sec*-propyl alcohol in the presence of an aluminium alkoxide (generally isopropoxide), which is an important reaction in laboratory practice:

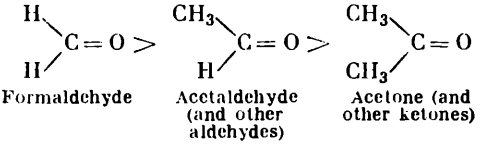


and the reduction of aldehydes and ketones with lithium aluminium hydride:



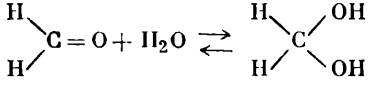
2. *Addition of organomagnesium compounds.* This typical and important reaction has also been discussed in the section concerned with alcohols. After the adducts are hydrolysed, primary alcohols are obtained from formaldehyde, secondary alcohols from other aldehydes, and tertiary from ketones.

3. *Addition of water.* According to the activity in reactions of addition to the carbonyl group, aldehydes and ketones are arranged in the following sequence:

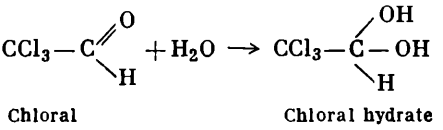


This is associated with the fact that the methyl and other alkyl groups have a greater tendency than the hydrogen atom to compensate for the positive charge on the carbonyl carbon atom (page 245). It is because of this that formaldehyde is the most active in addition reactions among the carbonyl compounds listed above. Still more active is trichloroacetaldehyde (chloral) since the CCl_3 group does not compensate at all for the positive charge on the carbonyl carbon but, on the contrary, draws electrons away from it.

Only the most active carbonyl compounds are capable of adding water. Formaldehyde in aqueous solutions is in the hydrated form:



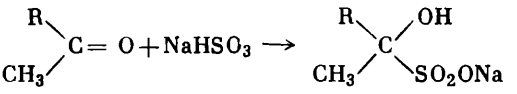
Liquid chloral adds water to form crystalline chloral hydrate:



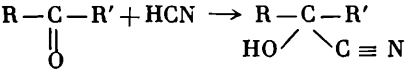
Chloral Chloral hydrate

Such hydrates behave as aldehydes in reactions.

4. *Addition of sodium bisulphite.* Aldehydes and ketones (of the type R—CO—CH_3 only) unite with sodium bisulphite to give so-called bisulphite compounds:

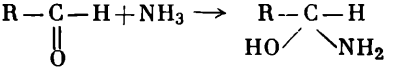


5. *Addition of hydrogen cyanide.* Hydrogen cyanide, HCN, adds on to aldehydes and ketones in the presence of a salt of hydrocyanic acid to give hydroxynitriles (cyanohydrins)*:

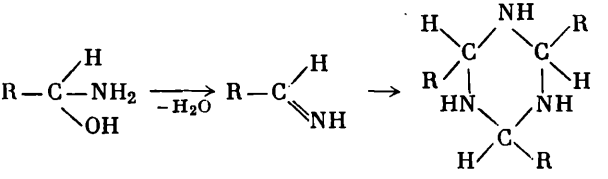


The cyanohydrins are useful in the synthesis of hydroxy acids and amino acids.

6. *Addition of ammonia.* Aldehydes add on ammonia to form **aldehyde ammonias**



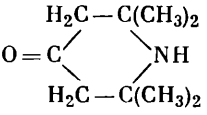
which readily lose water and are trimerized into heterocyclic compounds:



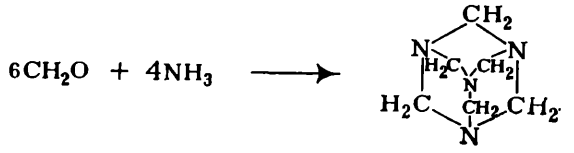
Ketones also react with ammonia but this reaction is complicated by the initial condensation. In the case of acetone, an unsaturated ketone—phorone—is formed first (page 401), which adds ammo-

* This reaction is referred to as the *cyanohydrin reaction.— Tr.*

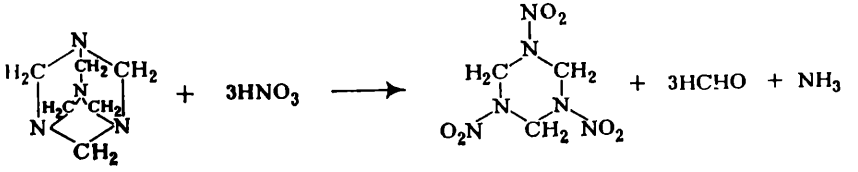
nia with the subsequent formation of a ring—a heterocyclic compound, namely, **triacetoneimine**:



Quite specific is the reaction of formaldehyde with ammonia, leading to **hexamethylenetetramine,** also known as **hexamine** or **urotropine** (A. M. Butlerov):



At room temperature in aqueous solution this reaction proceeds quantitatively. The shape of the urotropine molecule can be visualized if the central nitrogen atom, together with the methylene groups attached to it, is raised above the plane of the paper. Urotropine is used medicinally as such and in the form of a complex with $CaCl_2$ (calcex). It serves as a starting material for synthesizing an important explosive—hexogen (*cyclonite* or *cyclotrimethylenetrinitramine*) obtained by the reaction



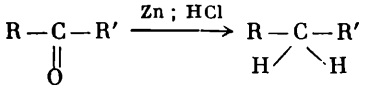
The reaction of formaldehyde with ammonia is already a substitution reaction, just as the second step of the reaction of ammonia with other aldehydes.

It should be noted that the replacement of oxygen in carbonyl compounds very often proceeds via the addition step.

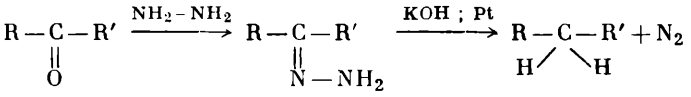
Replacement of the carbonyl oxygen. 1. Reactions of replacement of the oxygen atom of aldehydes and ketones by two chlorine atoms under the action of PCl_5 or by two fluorine atoms in the reaction with SF_4 have been considered on pages 163 and 98, respectively.

2. *Reduction of carbonyl compounds.* By the action of zinc amalgam in the presence of hydrochloric acid it is possible to replace

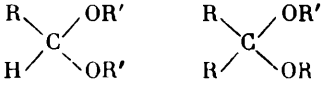
the carbonyl oxygen atom by two hydrogen atoms (**Clemmensen reduction**). This reaction has been worked out only for ketones:



Carbonyl compounds can also be reduced to the corresponding hydrocarbons by the **Wolff-Kishner method.** In this method, the hydrazone is first obtained (see page 179) and then heated with alkali in the presence of platinum:

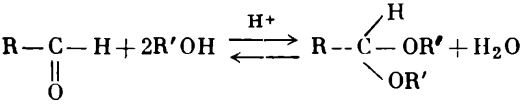


3. *Formation of acetals and ketals.* The reactions leading to the formation of the important functional derivatives of aldehydes and ketones—**acetals** and **ketals**—may be regarded formally as the replacement of the carbonyl oxygen by two alkoxyl groups, and the products obtained as the ethers of the ordinarily non-existent 1,1-glycols, $R_2C(OH)_2$:

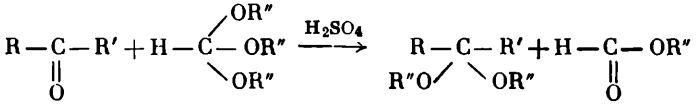


Acetal Ketal

Acetals are formed by direct interaction of aldehydes with alcohols in acid solution (a reversible reaction):

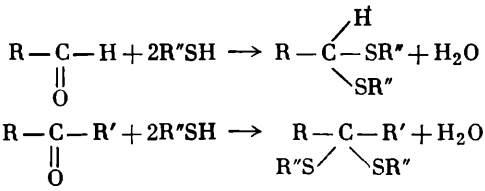


The ketals of monohydric alcohols do not result in this way. They are made most simply by the action of an orthoformate ester on ketones in the presence of a drop of concentrated sulphuric acid:



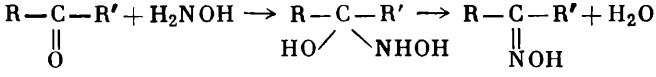
Like acetals, ketals are hydrolysed by aqueous acid to their parent ketones and alcohols.

The reaction of the analogues of alcohols—mercaptans, RSH, with aldehydes and ketones is analogous to the acetal formation:

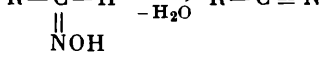


4. Especially important and diverse are the reactions of replacement of the carbonyl oxygen atom, which proceed by way of interaction between carbonyl compounds and nitrogen bases. These reactions constitute the second step of the addition reaction involving the elimination of water.

(a) Both aldehydes and ketones react with hydroxylamine. The resulting compounds are termed **oximes** and are distinguished as aldoximes or ketoximes, according as they are derived from aldehydes or ketones:

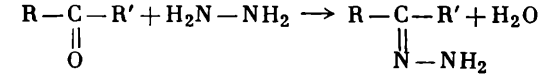


Under the action of dehydrating agents (P_2O_5) aldoximes are converted into acid nitriles:

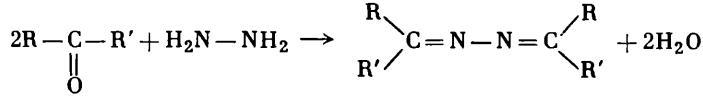


(b) With hydrazine the reaction takes different courses, depending on the ratio of the reactants.

The reaction with one molecule of a carbonyl compound yields **hydrazones**:

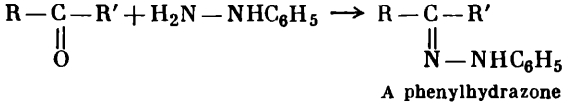


When two molecules are reacted with hydrazine, **azines** (aldazines and ketazines) result:



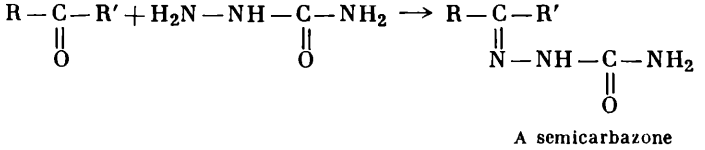
(c) With substituted hydrazines the formation of azines is impossible since only equimolecular amounts of reactants enter into the

reaction. The reaction with phenylhydrazine leads to **phenylhydrazones:**



A phenylhydrazone

The reaction with semicarbazides (see Volume II) gives **semicarbazones:**

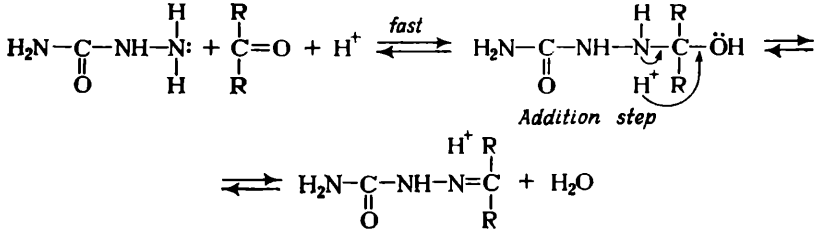


A semicarbazone

All these reactions proceed easily in aqueous solutions at room temperature in the presence of acetic acid. Oximes, hydrazones, azines and substituted hydrazones are readily hydrolysed in acid solution to their parent compounds.

As has already been pointed out, many of the reactions of replacement of oxygen in aldehydes and ketones constitute the second stage of the addition reaction (see page 177). A kinetic study of such reactions has shown that they are acid-catalysed even at the first stage, each reaction being characterized by its own optimum pH value. Here we are speaking of reactions with weak nucleophiles (such as aryl hydrazines, semicarbazide) since in reactions with strong nucleophiles (such as RSH, CN^- or $NaHSO_3$, which attacks the carbonyl in the form of the SO_3^{2-} ion) there is no need for proton catalysis because the carbonyl carbon is directly attacked by the reagent.

The catalytic action of the hydrogen ion* can be visualized as follows (using, as an example, the reaction with semicarbazide):



(the curved arrows indicate the formation of new bonds).

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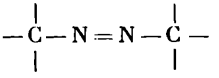
* Actually, the proton is always hydrated in aqueous medium and acts in the form of H_3O^+ (hydronium ion).

A similar route is followed by the first stage of reactions with other weak nitrogen bases and also with alcohols. With further increase of the concentration of hydrogen ions the starting nitrogen base becomes more completely bound (up to the complete protonation of the weakly basic molecule) and the reaction is stopped.

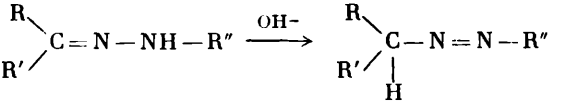
The reaction of addition at the carbonyl group is often catalysed also by bases, whose role consists in removing the proton being split off at the first step. In such cases the reaction proceeds without an intermediate addition of a proton to the carbonyl oxygen atom.

Substituted hydrazones of liquid aldehydes and ketones are normally solids which are easily identifiable by their melting points.

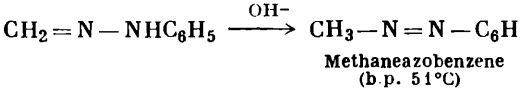
Hydrazones and substituted hydrazones when acted on by alkalis isomerize to azo compounds which are compounds containing the atomic grouping



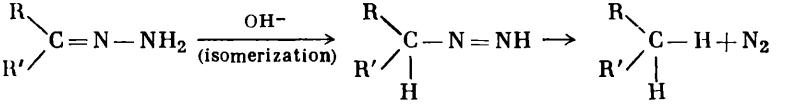
The scheme of such isomerization reactions is as follows:



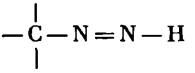
B. V. Ioffe was the first to succeed in preparing the monomeric phenylhydrazone of formaldehyde and isomerizing it to methaneazobenzene:



In the case of unsubstituted hydrazones, it is probably this preliminary isomerization that accounts for the Wolff-Kishner reaction which enables conversion of carbonyl compounds into the corresponding hydrocarbons:



since compounds of the type



are invariably unstable and decompose instantly according to the scheme

$$-\overset{|}{\underset{|}{C}}-N=N-H \longrightarrow -\overset{|}{\underset{|}{C}}-H+N_2$$

Oxidation. Aldehydes and ketones differ greatly in their behaviour towards oxidizing agents.

1. The aldehydes are oxidized both by strong ($H_2Cr_2O_7$, $KMnO_4$) and by weak oxidizing agents [$Ag(NH_3)_2^+$, Cu^{2+} in the form of Fehling's solution] to yield acids containing the same number of carbon atoms, the aldehyde group being converted to a carboxyl group:

$$R-\overset{\overset{O}{\|}}{C}-H+O \longrightarrow R-\overset{\overset{O}{\|}}{C}-OH$$

2. The ketones are oxidized only by strong oxidizing agents on heating. For example, acetone dissolves well potassium permanganate in the cold, no interaction being observed. The oxidation takes place at a higher temperature with rupture of the carbon chain on both sides of the carbonyl, a mixture of four acids being obtained in the general case (Popov's rule):

$$CH_3-CH_2-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-CH_2-CH_3+O \longrightarrow$$

$$\longrightarrow CH_3-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-OH+CH_3-CH_2-\overset{\overset{O}{\|}}{C}-OH+$$

$$+CH_3-CH_2-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-OH+CH_3-\overset{\overset{O}{\|}}{C}-OH$$

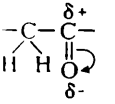
Aldehydes can most simply be distinguished from ketones by their reaction with an ammoniacal solution of silver oxide, from which a precipitate of metallic silver is formed by the action of aldehydes.

3. In contrast to ketones, aldehydes when reacted with a number of alkoxides, say, with $(RO)_3Al$ or $(RO)_4Ti$, undergo an industrially important reaction: one molecule of an aldehyde is reduced due to the oxidation of another molecule and an ester is formed as a result **(Tishchenko reaction):**

$$2CH_3-\overset{\overset{O}{\|}}{C}-H \xrightarrow{Al(OCH_3)_3} CH_3-\overset{\overset{O}{\|}}{C}-O-CH_2-CH_3$$

The Tishchenko reaction involves the hydride transfer of the hydrogen of the aldehyde group.

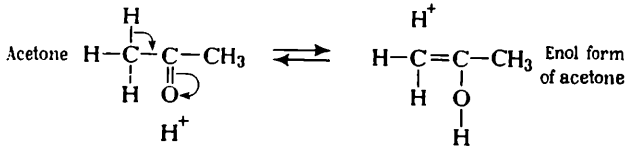
Substitution in the α-Position. The polarizability of the π-bond of the carbonyl group and the presence of a partial positive charge on the carbonyl carbon atom (see page 169) affect the behaviour of the hydrogen atoms of the next-to-carbonyl hydrocarbon radical (α-linkage) of aldehydes and ketones. Naturally, in the system



(δ+ and δ— signify a partial charge, i.e., a fraction of the full electron charge)

the hydrogen atoms are held less firmly under the influence of the neighbouring δ+ charge than in hydrocarbons and are more readily removed in the form of protons from the molecule. When a positively charged centre (of an electrophilic reagent) approaches the carbonyl oxygen atom, a further shift of the π-electrons of the carbonyl double bond to the oxygen takes place, which weakens the C—H bond still further and facilitates the ionization of the hydrogen. In the system given above the H—C—C=O bonds are conjugated (σ-π-conjugation) and the system of these bonds acts as a whole: the rupture of the C—H bond (under the action of bases that pull the proton) leads to the cleavage of the C=O π-bond and to the concentration of the π-pair of electrons at the oxygen. And, conversely, the attack on the oxygen which breaks the π-bond often results in the expulsion of a proton.

1. *Enolization.* One of the manifestations of these relations is the enolization reaction characteristic of aldehydes and ketones containing α-hydrogen atoms:



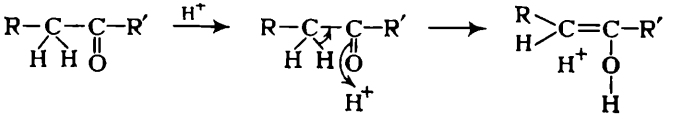
For the equilibrium in aldehydes and ketones to be displaced considerably far to the right—in the direction of the enol form, it is necessary, however, that the hydrogen atom be still more mobile (more activated), which is achieved when one of the α-hydrogen atoms is replaced by any other group that pulls the electrons (an electron-attracting, or electrophilic, group), say, the second carbonyl.

At room temperature acetone contains only 2.5×10^{-4} per cent of the enol form. Incidentally, the rate of many of the reactions of ketones which involve the replacement of the hydrogen atom in the α hydrocarbon link is equal to the rate of enolization and is independent of the concentration of the attacking reagent. An example is the bromination reaction leading to the formation of α-bromoketone.

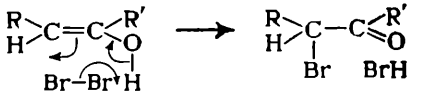
The rate of bromination is zero-order with respect to bromine, i.e., does not depend on the concentration of bromine and is determined by the rate of enolization alone. Since the enol reacts with bromine much faster than does the enolization proceed, the rate-determining step will be, as is always the case, the slower reaction, namely, enolization. This is verified by the fact that chlorination and iodination occur at the same rate as bromination.

The following reaction mechanism is quite plausible:

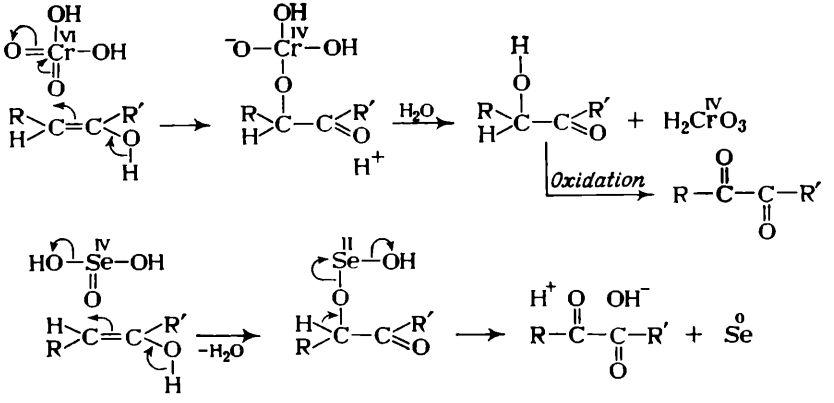
(a) enolization effected by an acid



(b) *concerted* bromination



The oxidation of ketones by chromic acid* or selenium dioxide to 1,2-dicarbonyl compounds proceeds in a similar way:



Thus, ketones can be oxidized to α-carbonyl and α-dicarbonyl compounds via the enolization step. In both cases, however, the rate of oxidation is first-order with regard to both the oxidizing agent and the ketone (i.e., is proportional to the concentrations of both components). This means that the slowest step that determines the overall

* Compare the reaction given on page 170.

rate of the reaction is not the enolization but evidently the stage at which the ester enol and the oxidant anion are formed.

2. *Nef methylation.* Since ketones, in contrast to aldehydes, are rather stable towards bases, they can be methylated by methyl iodide at the α-linkage in the presence of potassium hydroxide or sodamide:

$$R-\overset{\overset{O}{\|}}{C}-CH_3 + KOH + CH_3I \longrightarrow \begin{cases} R-\overset{\overset{O}{\|}}{C}-CH_2-CH_3 \\ R-\overset{\overset{O}{\|}}{C}-CH(CH_3)_2 \\ R-\overset{\overset{O}{\|}}{C}-C(CH_3)_3 \end{cases}$$

The reaction, no doubt, consists of the expulsion of a proton by alkali and electrophilic attack on the mesomeric ketone anion by methyl iodide.

In this anion, the negative charge is not fixed on the carbon atom on which it has originated but is distributed between this carbon atom and the oxygen. This can be depicted in two ways:

$$R-\overset{\overset{O}{\|}}{C}-\bar{C}H_2 \quad or \quad R-\overset{\overset{O}{\|}}{C}-\bar{C}H_2 \longleftrightarrow R-\overset{\overset{O^-}{|}}{C}=CH_2$$

The phenomenon of mesomerism will be discussed later on (see pages 235 and 318).

Under severe conditions (350°C), however, solid alkali splits ketones with the formation of an acid and a hydrocarbon. When acted on by alkali, ketones of the general formula $C_nH_{2n+1}COCH_3$ form largely an acid salt, $C_nH_{2n+1}COONa$, and methane:

$$C_nH_{2n+1}COCH_3 + NaOH \longrightarrow C_nH_{2n+1}COONa + CH_4$$

3. *Formation of oximes.* The action of nitrous acid on ketones is of interest:

$$R-\overset{\overset{O}{\|}}{C}-CH_2-CH_3 + HO-N=O \xrightarrow[-H_2O]{} R-\overset{\overset{O}{\|}}{C}-\underset{\underset{N=O}{|}}{CH}-CH_3 \rightleftarrows R-\overset{\overset{O}{\|}}{C}-\overset{\overset{NOH}{\|}}{C}-CH_3$$

The nitroso group (—N=O) of nitrous acid displaces the mobile α hydrogen atom of the ketone, as a result of which the second α hydrogen atom is found to be influenced not only by the carbonyl group but also by the more electron-attracting nitroso group. Under this influence it leaves its place at the carbon atom and migrates not to the carbonyl oxygen but to the more nucleophilic (more precisely,

protophilic) oxygen atom of the nitroso group. An oxime grouping is formed as a result.

Oximes are hydrolysed in acid medium:

$$R-\underset{\underset{O}{\|}}{C}-\underset{\underset{N-OH}{\|}}{C}-CH_3+H_2O \xrightarrow{H^+} R-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-CH_3+NH_2OH$$

The hydrolysis shows that the compound formed by the interaction of a ketone with nitrous acid is a monoxime of a diketone (2,3-butanedione, or diacetyl, in the case of $R=CH_3$). If this diketone or its monoxime is acted on by hydroxylamine, dimethylglyoxime will be formed by the familiar reaction:

$$CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{N-OH}{\|}}{C}-CH_3+H_2NOH \longrightarrow CH_3-\underset{\underset{HON}{\|}}{C}-\underset{\underset{NOH}{\|}}{C}-CH_3+H_2O$$

Dimethylglyoxime is the well-known Chugaev reagent for the nickel cation.

In the case of difficultly hydrolysable oximes, the oxime group can be removed and the carbonyl compound regenerated through its oxidation by $NH_4NO_3 \cdot Ce(NO_3)_4$ in a medium of lower alcohols or acetic acid at a temperature of —40 to 0°C.

4. *Halogenation.* The mobility of an α-hydrogen atom is also exhibited on halogenation. Under the action of a free halogen, aldehydes and ketones are readily chlorinated, brominated and even iodinated at the alpha-position (as pointed out above, the reaction proceeds via the enol form). With an excess of halogen all the α-hydrogen atoms can be replaced by halogen:

$$CH_3-\overset{\overset{O}{\|}}{C}-H+Cl_2 \longrightarrow \underset{\text{Chloroacetaldehyde}}{ClH_2Cl-\overset{\overset{O}{\|}}{C}-H}+HCl$$

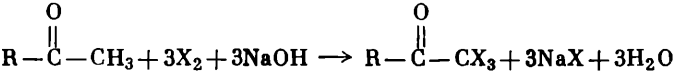
$$CH_3-\overset{\overset{O}{\|}}{C}-H+3Cl_2 \longrightarrow \underset{\text{Chloral}}{CCl_3-\overset{\overset{O}{\|}}{C}-H}+3HCl$$

$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3+Cl_2 \longrightarrow \underset{\text{Monochloroacetone}}{ClCH_2-\overset{\overset{O}{\|}}{C}-CH_3}+HCl$$

$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3+3Cl_2 \longrightarrow \underset{\text{Trichloroacetone}}{CCl_3-\overset{\overset{O}{\|}}{C}-CH_3}+3HCl$$

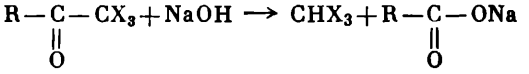
The reaction is catalysed both by acids (a hydrogen ion) and, notably, by bases. In the case of chlorination, bromination or iodination in alkaline medium, the products of the first stage of haloge-

nation cannot be isolated because the reaction immediately proceeds on to the third stage:



where R = H or alkyl.

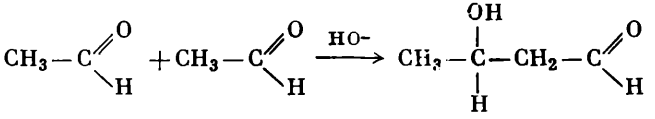
Carbonyl compounds of this kind are unstable in alkali and immediately undergo a **haloform cleavage** to yield a salt of a carboxylic acid, RC(=O)ONa, and haloform:



In practice, haloforms, i.e., chloroform, $CHCl_3$, bromoform, $CHBr_3$, or iodoform, CHI_3, are made by halogenation in an alkaline solution of acetone or ethanol (the latter is oxidized first to acetaldehyde under these conditions).

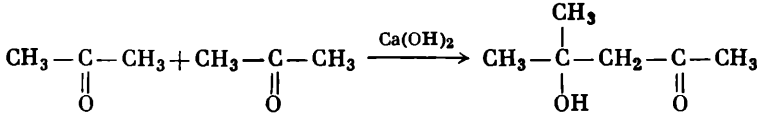
5. *Condensation.* When aldehydes and ketones undergo condensations, the α-methylene group of one molecule and the carbonyl group of a second become simultaneously involved in the reaction. Aldehydes enter into these reactions more readily than ketones, this time under the influence of a weak alkali or dilute acid.

The first stage of the reaction is the **aldol condensation** which proceeds by way of addition of the α-linkage of one molecule of the carbonyl compound to the carbonyl group of the other molecule. Two molecules of acetaldehyde combine to yield an open-chain compound, aldol (*ald*ehyde-alcoh*ol*):



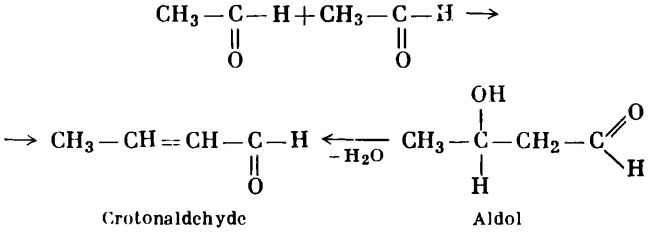
Hence the name of aldol condensation.

The aldol condensation of acetone results in the formation of diacetone alcohol:



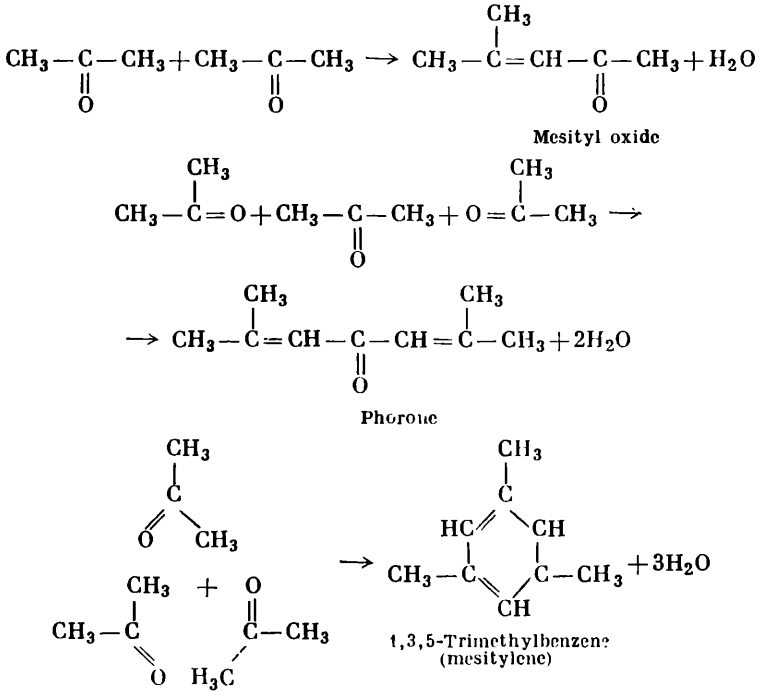
Under more drastic conditions, the water is eliminated from the products of this reaction and an unsaturated carbonyl compound is

formed (crotonaldehyde from acetaldehyde), but the intermediate hydroxy compound cannot usually be isolated:



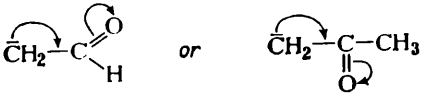
This reaction is known as the **croton condensation.**

The condensation of acetone proceeds, in particular, through its interaction with sulphuric acid of varying concentration. The last of the reactions given below is accompanied by the evolution of all the oxygen in the form of water and is remarkable for the formation of an aromatic hydrocarbon—1,3,5-trimethylbenzene which is also known as mesitylene:

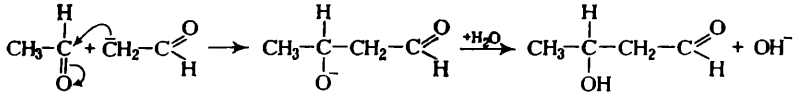


The fact that the aldol condensation is catalysed both by an acid and by a base is accounted for by the following reaction mechanism:

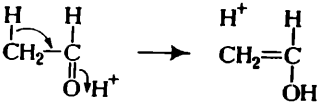
(a) the catalysis effected by alkali consists in that the OH^- group pulls H^+ away from the α-linkage of the carbonyl compound and the resulting anion (carbanion)

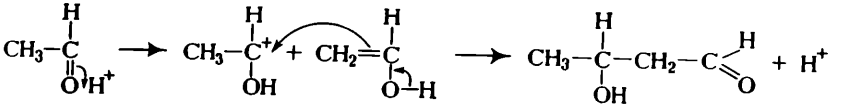


attacks the carbonyl carbon of the other molecule:



(b) on acid catalysis the hydrogen ion brings about the enolization of one molecule of the carbonyl compound and the formation of a carbonium ion from the other:

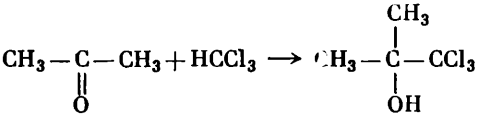




Carbonium ion Enol

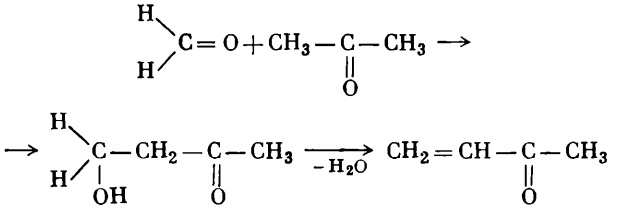
The curved arrows in these equations indicate the shift of electrons which occurs partly in the molecule before the reaction takes place and ends in the reaction with the formation of new bonds, the original ones being ruptured.

The aldol- or croton-type condensations may take place not only between two molecules of identical carbonyl compounds, but also between two different aldehydes, two ketones, or between an aldehyde and a ketone, and even between carbonyl compounds and hydrocarbon derivatives of the type $R—CH_2—X$, where X is a strong electron-attracting group ($>C=O$, $—NO_2$, $>SO_2$, $—CCl_3$). An example is the reaction between acetone and chloroform, in which the three chlorine atoms joined together have strongly activated the hydrogen:

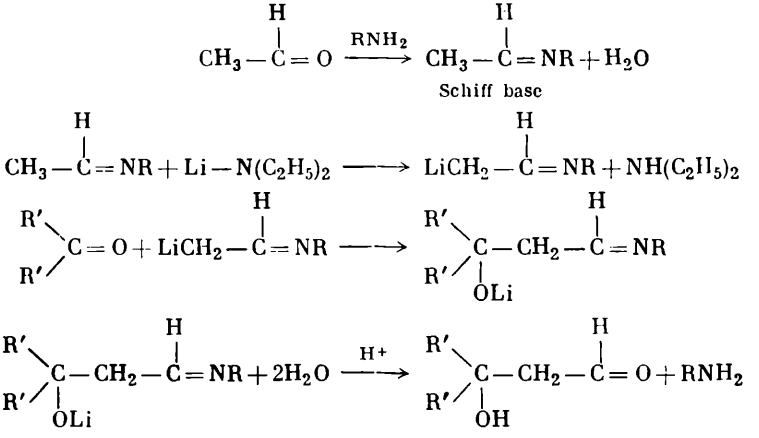


These reactions are of great importance in synthesis.

Formaldehyde which has no α-linkage cannot enter into such reactions. The condensation of its molecules takes a different route and leads to the formation of a mixture of carbohydrates (see Volume II). With other carbonyl compounds, formaldehyde is condensed in a normal fashion, for example,



The carbonyl group of an aldehyde is more active than that of a ketone, so that when aldehydes are condensed with ketones the aldehyde carbonyl always adds on the elements of the α-linkage of the ketone. Of interest is the method of preparation of aldols from ketones suggested by Wittig. For a condensation with ketones Wittig made use of nitrogen derivatives of aldehydes—**Schiff's bases**—in the form of lithium compounds:



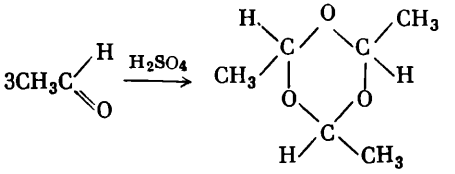
As the result of these conversions, the ketone R'_2CO enters, as it were, into an aldol condensation with the aldehyde. The type of reaction is the same as in the interaction between a ketone and a Grignard reagent or a lithium alkyl, the only difference being that the organometallic reagent is prepared by direct metalation* of the readily replaceable α-hydrogen of the Schiff base.

---

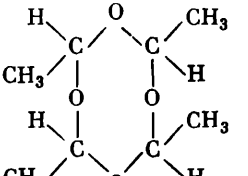
* Metalation is a substitution reaction (*metal-hydrogen exchange*).— *Tr.*

6. *Polymerization.* Polymerization reactions are characteristic only of the aldehydes of the series under consideration. Ketones do not polymerize under any normal conditions.*

An example of an ordinary type of aldehyde polymerization is the polymerization of acetaldehyde. When acetaldehyde is mixed with a drop of sulphuric acid, an exothermal reaction takes place, with boiling of acetaldehyde, which is trimerized into a six-membered heterocyclic compound—**paraldehyde**. If the polymerization is conducted at temperatures below 0°C, tetramerization occurs and solid **metaldehyde** is formed, which is utilized as a fuel to replace alcohol:



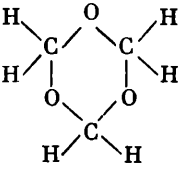
Paraldehyde (b.p. 124 °C)



Metaldehyde (sublimes at 112°C)

Both polymers are readily depolymerized if they are heated with a drop of sulphuric acid and the resulting acetaldehyde (b.p. 21°C) is distilled off.

Formaldehyde in the gaseous phase undergoes spontaneous polymerization into a crystalline trimer, trioxane or trioxymethylene, which is a lower homologue of paraldehyde:



Trioxymethylene
(m.p. 62°C)

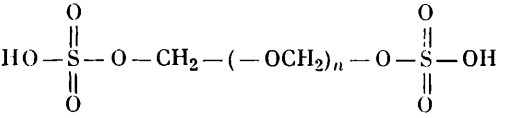
When a 40-percent aqueous solution of formaldehyde (**formalin**) is allowed to stand, a spontaneous precipitation of polymers of a different type takes place. The polymers thus precipitated are linear high-molecular-weight compounds:

$$(n+1)CH_2O + H_2O \longrightarrow HOCH_2-(-OCH_2-)_n-OH$$

in which n is equal to several tens or hundreds. These polymers are known as **polyoxymethylenes** or **paraform**. They also differ by their terminal groups: when polymerization is caused by addition of sul-

* Only in recent years have V. A. Kargin and his coworkers succeeded in polymerizing, under special conditions, acetone into a high-molecular-weight product (linear polymerization).

phuric acid, the ester sulphate groups appear at both ends of the chain:



If methyl alcohol (methanol) is present in formaldehyde (as is usually the case in commercial formalin), methoxyl groups may appear at the ends of some polymer molecules:

$$CH_3OCH_2-(-OCH_2-)_n-OCH_3$$

Thus, paraformaldehyde, or paraform, is a mixture of compounds differing not only in molecular weight but also (insignificantly in terms of percentage content) in composition. Under the action of aqueous alkali it depolymerizes to formaldehyde.

Chemists have recently succeeded in polymerizing dry formaldehyde into polyformaldehyde of a much higher molecular weight. The requirement set forth to the polymerization accomplished at the present time on an industrial scale is the high purity of formaldehyde. Polyformaldehyde is one of the cheapest plastics having valuable properties, which is used for the manufacture of machine parts. As demonstrated by N. S. Enikolopov, the same product can be prepared by polymerization of trioxymethylene.

II. Polymers and Polymerization

Strictly speaking, a polymer of a particular compound is a substance having the same composition but a multiple molecular weight, irrespective of the structure of the starting material and the end product. Dimers, trimers, tetramers, etc., and polymers proper are distinguished. Examples of trimers and tetramers have already been cited in considering aldehydes and ketones. Aldol is essentially a dimer of acetaldehyde. Other examples of polymers are: benzene, C_6H_6, with respect to acetylene, C_2H_2; butylene, C_4H_8, with respect to ethylene, C_2H_4.

Polymerization is the formation of a polymer from a monomer. The term monomer makes sense only with respect to its polymer. If there is no polymer, there is no monomer. The historical connotation of the terms *polymer* and *polymerization*, however, varied with time. First, it is in the field of aldehydes and ketones that the concept of polymerization was contrasted to that of condensation. Condensation (aldol or croton) is characterized by the formation of a new carbon-carbon bond. Polymerization was defined, in this narrow

sense, as the binding of monomer molecules by non-carbon bonds into a polymeric molecule which can easily be depolymerized. Because of the obvious kinship between polyoximethylenes and other polymers of aldehydes and also of the insufficient accuracy of ordinary quantitative analysis which could not detect the presence of terminal groups (the end groups for polyoxymethylenes are HO—, CH_3O— or $HOSO_2O$—), compounds of this kind were also called polymers and the process of their formation was termed polymerization, and this term was extended to all similar linear high-molecular-weight compounds, no matter whether the monomers are bound by carbon-carbon or other bonds. This is generally accepted at present, though such linear high-molecular-weight compounds may be regarded as the polymers of a given monomer only if the presence of end groups is ignored (strictly speaking, their presence is often not established). For example, polyethylene (polythene) (see page 348) which is produced by the polymerization of ethylene in the presence of oxygen and which has the structure $HO—(CH_2CH_2)_n—OH$ is called a polymer of ethylene. Other examples of linear polymers include the series of polyglycols made by the action of ethylene oxide on ethylene glycol in acid solution (page 159):

$$\left.\begin{array}{l} HOCH_2CH_2-O-CH_2CH_2OH \\ HOCH_2CH_2-O-CH_2CH_2-O-CH_2CH_2OH \\ HOCH_2CH_2-(-O-CH_2CH_2-)_n-O-CH_2CH_2OH \end{array}\right\} \begin{array}{l}\text{The polymer-homologous}\\ \text{difference is}\\ -OCH_2-CH_2-\end{array}$$

Series of this kind constitute a series of polymer homologues (not to be confused with homologues). Polymer homologues differ from one another by one or more monomeric units built into the chain. Let us take, as an example, the polymer-homologous series for paraform:

$$\left.\begin{array}{l} HOCH_2-(-OCH_2-)_{n-1}-OH \\ HOCH_2-(-OCH_2-)_n-OH \\ HOCH_2-(-OCH_2-)_{n+1}-OH \end{array}\right\} \begin{array}{l}\text{The polymer-homologous difference is}\\ -OCH_2-\end{array}$$

Linear polymers of a very high molecular weight have assumed great technical importance and will be considered under "Olefins" (page 346).

D. Uses of Aldehydes and Ketones

Formaldehyde in the form of a nearly 40-percent aqueous solution containing 5-8 per cent of methanol is produced in large quantities by the catalytic oxidation of methanol. This is the so-called formalin. An ever increasing amount of formaldehyde is also made by direct controlled oxidation of methane or cracked hydrocarbons. Because of the toxicity of formaldehyde for all organisms it is used in the form of dilute aqueous solutions as a disinfectant, for treating seeds (in order to kill darnel spores), etc. The major proportion of formaldehyde is used for production of the various plastics, varni-

shes and glues based on phenol-formaldehyde resins (see Volume III) and also on urea- and melamine-formaldehyde resins. Its use for preparation of urotropine and an explosive (hexogen) has already been considered (page 177).

Acetaldehyde prepared from acetylene serves as an important intermediate in industrial syntheses of alcohol, acetic acid, ethyl acetate (the Tishchenko reaction), crotonaldehyde, butyraldehyde and a number of other products.

Acetone is one of the most multi-tonnage solvents. It is produced industrially together with phenol via cumene hydroperoxide. Acetone is also used for synthesis of methacrylic acid and its methyl ester, methyl methacrylate (through the addition of hydrocyanic acid and elimination of H_2O; see page 409), which is used as a monomer in the production of plexiglas. Acetone is subjected to cracking to produce ketene, $CH_2=C=O$ (see page 406), which is reacted with acetic acid to obtain acetic anhydride and other derivatives of acetic acid.

Methyl ethyl ketone is widely used as a solvent and also for the manufacture of diacetyl and its oxime—dimethylglyoxime.

2.8. Dialdehydes, Ketoaldehydes and Diketones

These compounds are classified according to the number of carbon atoms in the carbon chain, which separate two carbonyl groups. If this number is equal to zero, i.e., if the two carbonyl groups are joined directly to each other, such compounds are called 1,2- or α-dicarbonyl compounds; if there is one separating link, they are given the name 1,3- or β-dicarbonyl compounds, and so on.

The physical properties and formulas of the simplest dicarbonyl compounds are given in Table 2.12.

A. Preparation of Dicarbonyl Compounds

α-Dicarbonyl compounds. Owing to the high reactivity of the α-methylene group of aldehydes and ketones, it can be converted to a carbonyl group largely in two ways: by oxidation with selenium dioxide (a relatively new route, Reilly, 1932):

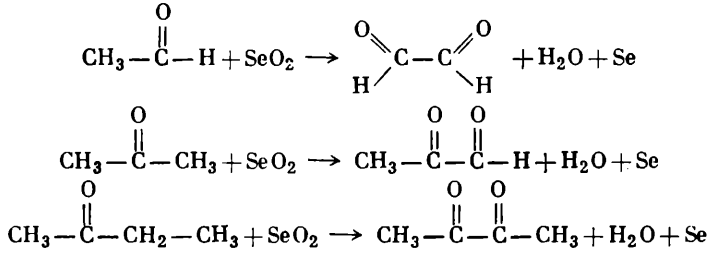
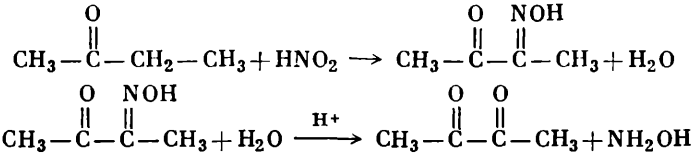


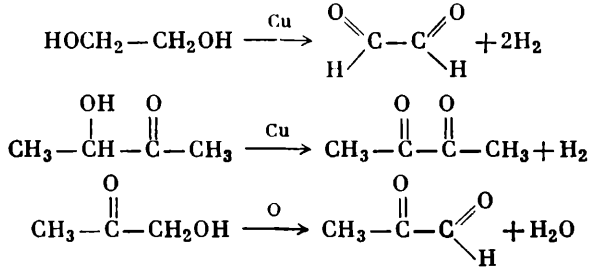
TABLE 2.12. **Dicarbonyl Compounds**

Formula	Name		m.p., °C	b.p., °C	Density d_4^{20}	Remarks
	trivial	Geneva				
OHC—CHO	Glyoxal	Ethanedial	15	50.4	1.14	Green vapours or yellow crystals
$OHC-CH_2-CHO$	Malondialdehyde	Propanedial	—	—	—	Extremely unstable; above 0°C polymerizes
$OHC-CH_2CH_2-CHO$	Succindialdehyde (succinaldehyde)	Butanedial	1.4	170	1.064	—
$CH_3-CO-CO-CH_3$	Diacetyl or dimethylglyoxal	Butane-2,3-dione	−2.4	88	0.980 (d_{15}^{15})	Greenish-yellow liquid
$CH_3CO-CH_2-COCH_3$	Acetylacetone	Pentane-2,4-dione	−23.2	139 (at 746 mm Hg)	0.976	Colourless liquid
$CH_3CO(CH_2)_2COCH_3$	Acetonylacetone	Hexane-2,5-dione	−9	194	0.970	—
$CH_3-CO-CHO$	Pyrotartaraldehyde	Propanonal	—	72	1.045 (at 24°C)	Yellow liquid

and by the action of nitrous acid on ketones (see page 185). The resulting isonitroso ketones are nothing more than the monoximes of α-dicarbonyl compounds; on hydrolysis they give α-diketones:

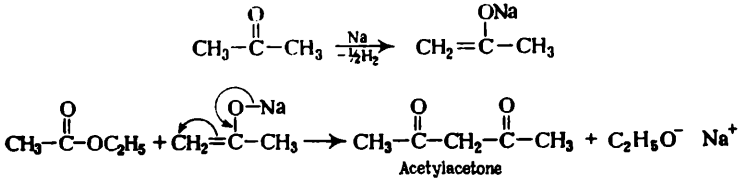


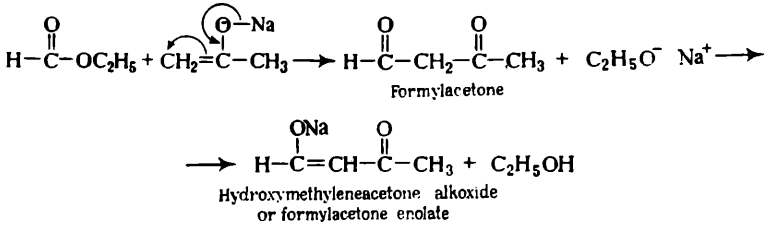
Apart from being prepared from monocarbonyl compounds, α-dicarbonyl compounds can be synthesized by using ordinary methods of oxidation or catalytic dehydrogenation of primary alcoholic groups (for preparation of aldehyde groups) or secondary alcoholic groups (for preparing keto groups). Since α-glycols and α-hydroxycarbonyl compounds are the most available materials, this route is most suitable for the synthesis of α-dicarbonyl compounds:



β-Dicarbonyl compounds. The most important route for synthesis of β-dicarbonyl compounds is the condensation of ketones with carboxylic acid esters by the action of metallic sodium. In the case of an ester of formic acid the reaction results in the formation of a β-aldehyde ketone; when homologous esters are used, β-diketones are obtained. The simplest β-dialdehyde, malondialdehyde ($OHC—CH_2—CHO$), is extremely unstable and cannot be made in this way.

The overall equation for the condensation process is formulated as follows:

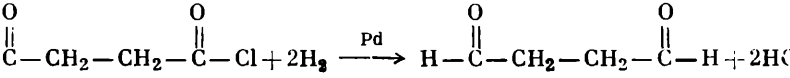




Because of the sharply increased mobility of the protons of the central α-methylene linkage in a β-dicarbonyl compound, the latter is isolated in both reactions in the form of a sodium derivative of the enol form. For example, the resulting β-aldehyde ketone, formylacetone, when reacted with sodium ethoxide is immediately converted into the sodium alkoxide of hydroxymethyleneacetone (the same happens with acetylacetone). In contrast to acetylacetone, free formylacetone is incapable of long existence and is trimerized by a croton-like condensation to triacetylbenzene (for the properties of dicarbonyl compounds, see below).

The more detailed mechanism of this important reaction will be treated in the discussion of an absolutely analogous ester condensation of two molecules of an ester (see Volume II).

γ-Dicarbonyl compounds. γ-Dialdehydes can be prepared by reduction of dichloro anhydrides of the corresponding acids (Rosenmund):



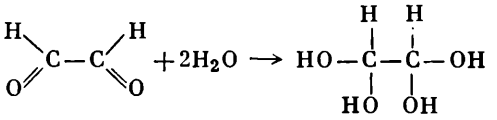
γ-Diketones are made either by the action of chloroacetone on sodioacetoacetic ester (Volume II) followed by the ketonic cleavage of the resulting acetonylacetoacetic ester or by the reaction between iodine and sodioacetoacetic ester with the subsequent acid cleavage of the diacetylsuccinic ester obtained (see Volume II).

II. Properties of Dicarbonyl Compounds

All dicarbonyl compounds can of course be reduced to the corresponding glycols, and dialdehydes oxidized to the corresponding dibasic acids. There is no point in dwelling here on these obvious reactions, but the student majoring in organic chemistry must ascertain the relations of dicarbonyl compounds to their reduction and oxidation products—glycols, acids, hydroxy acids and aldehydic and ketonic alcohols. We shall consider only the specific conversions of dicarbonyl compounds.

α-Dicarbonyl compounds have very reactive carbonyl groups, especially dialdehydes, due to the neighbourhood of two electron-attracting groups. For example, glyoxal, like chloral and formal-

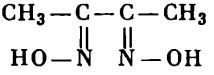
dehyde, adds in aqueous solution one molecule of water to each aldehyde group:



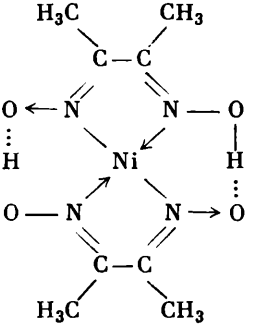
and changes from yellow to colourless. Glyoxal undergoes an internal Cannizzaro reaction (see Volume III) with alkali to give glycolic acid:

$$CHO-CHO+NaOH \longrightarrow CH_2OH-COONa$$

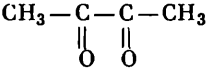
The most interesting derivatives of α-dicarbonyl compounds are dioximes which form inner complexes with a number of metal cations, for example, dimethylglyoxime (diacetyldioxime):



which with nickel gives a crimson-red insoluble precipitate*:



The diacetyl (or biacetyl) itself



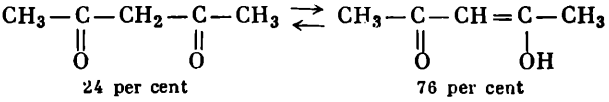
is one of the principal components of a mixture of substances responsible for the odour of butter (tenths of a milligram per 1 kg of butter), and is therefore added to margarine and synthetic butter.

α-Dicarbonyl compounds are used in the synthesis of heterocycles (see Volume III).

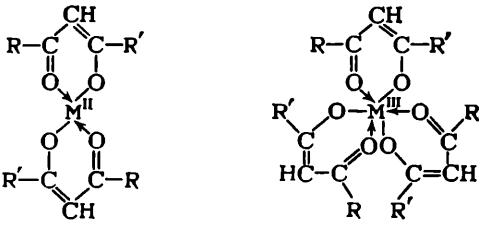
β-Diketones (1,3-diketones) are characterized mainly by the ease with which the hydrogen atoms of the central methylene group

* In the formula of nickel dimethylglyoxime the arrow in N → O indicates a semi-polar bond (see page 30) and the one in N → Ni, a donor-acceptor bond (formed by the unshared electron pair of trivalent nitrogen); the three dots stand for hydrogen bonds.

are ionized (the increased acidity of these hydrogens). It is because of this increased acidity that β-diketones are prone to undergo reactions of replacement of these hydrogen atoms and of condensation at the methylene group. This increased acidity is also responsible for the high degree of enolization (see Volume II):



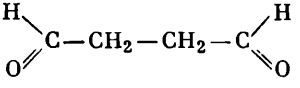
β-Diketones form stable inner-complex enolates of divalent and trivalent metals:



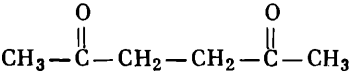
The carbonyl oxygen atom in β-diketones supplies a pair of electrons to the metal of the alkoxide (enolate) of the enol form of the diketone. Thus, the divalent metal is found to be linked to four oxygen atoms (the four coordination sites around the metal are occupied)—two enolic and two ketonic oxygens. The coordination number of the trivalent metal is 6 and the number each of enolic and ketonic oxygens is 3. Such inner-complex compounds of acetylacetone—with copper, chromium(III), iron(III), and cobalt(III)—are very stable, water-insoluble, coloured crystalline substances. Their colour is different from the colour of the corresponding metal cation. They dissolve well in organic solvents—acetone, chloroform, benzene. Inner-complex heterocyclic compounds of this kind (metal and oxygen—heteroatoms) are also called **chelate compounds** (the word *chelate* is derived from the Greek, meaning a claw, as of a lobster): a diketone surrounds a metal, like a claw. Some diketones of this type are used to extract a metal cation (say, uranium) by an organic solvent from dilute aqueous solutions.

β-Diketones find application in the synthesis of six-membered heterocycles.

Among γ-dicarbonyl compounds, succindialdehyde has found extensive use in laboratory synthesis, particularly in the synthesis of heterocyclic compounds. It has the following formula:



The same purpose is achieved by using the simplest representative of γ-diketones (1,4-diketones), acetonylacetone (2,5-hexanedione),



γ-Diketones are not enolized to the same extent as β-diketones and do not form chelate compounds.

III. Acids

The concept of acids and bases in organic chemistry does not differ from the corresponding concepts in inorganic chemistry. It is necessary, however, to remind the reader that there exist several definitions of acids, which differ in degree of generalization.

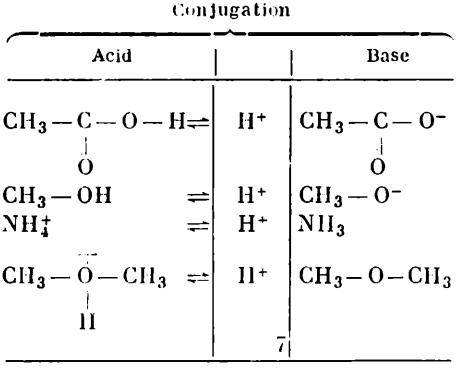
The classical definition of an acid states: An acid is a substance which dissociates electrolytically with the formation of a hydrogen ion. A base is a substance which binds the hydrogen ion into an undissociated (or slightly dissociated) molecule.

According to the Brönsted-Lowry definition, an acid is a substance* that can give a proton. The second product that is formed in this process is called a base. Thus, there is the following relation:

$$\text{Acid} \rightleftharpoons H^+ + \text{Base}$$

The base that has accepted the proton is converted into the acid which is called the **conjugate acid** of that base. And, conversely, we may speak of the conjugate base of the given acid.

Examples of acids and bases according to the Brönsted-Lowry definition are as follows:



* In these definitions the word "substance" is interpreted very broadly to mean any species of molecule or ion capable of undergoing reaction.— *Tr.*

An even more generalized concept of acids and bases is found in the Lewis definitions. All substances (neutral molecules or anions) possessing a free pair of electrons and capable of supplying it for bond formation are called bases. The supply by such substances of a pair of electrons for the formation of a bond with a proton is a special case which fits into the Brönsted-Lowry definition of acids and bases. All substances that lack a pair of electrons for their electron shell to be stable are called acids. Examples of Lewis acids are:

Acid	Base	Salt-like substance
H^+	$CH_3-\overset{\overset{O}{\|}}{C}-O^-$	$CH_3-\overset{\overset{O}{\|}}{C}-OH$
H^+	HO^-	H_2O
BF_3	$(C_2H_5)_2O$	$(C_2H_5)_2\overset{+}{O}:\bar{B}F_3$
$AlCl_3$	Cl^-	$AlCl_4^-$
$ZnCl_2$	HO^-	$ZnCl_2OH^-$
$FeCl_3$	Cl^-	$FeCl_4^-$

Thus, in using the terms "an acid" and "a base" one has to specify what he means. If no reservations are made, these terms are considered to be used in the classical sense. The term "a conjugate acid" implies the Brönsted-Lowry concept of an acid. In those cases when we speak of substances lacking a pair of electrons, we mean a Lewis acid.

As known from a course of general chemistry, the strength of acid HX is measured by means of the dissociation constant K_a (or the acidity constant) which is defined by the equation

$$K_a = \frac{a_{H^+}a_{X^-}}{a_{HX}} = \frac{\gamma_{H^+}[H^+]\gamma_{X^-}[X^-]}{\gamma_{HX}[HX]}$$

where $[H^+]$, $[X^-]$ and $[HX]$ are the concentrations; a with the corresponding subscripts are activities; γ with the same subscripts are activity coefficients of the corresponding ions or molecules. The products of activity coefficients (which can be found from tables) by concentrations (see page 110) give activities. In dilute aqueous solutions, the activity coefficients for weak electrolytes are equal to unity and the expression for the dissociation constant assumes the following form:

$$K_a = \frac{[H^+][X^-]}{[HX]}$$

Ordinarily, the values of dissociation constants are much less than unity; for example, the dissociation constant of acetic acid in water at 25°C is 0.0000176, which is more conveniently written as 1.76×10^{-5}, and still better as $10^{-4.75}$. With this notation it is particularly convenient to compare the strengths of various acids through a comparison of the exponents for 10. For the sake of simplicity, the minus sign is omitted. Taken with the positive sign, the negative exponent (in other words, the decimal or common logarithm) is designated as pK_a. In the example given, $pK_a = 4.75$. The basicity of bases can be compared by measuring the K_a values of conjugate acids (for example, in the case of ammonia the dissociation constant of the NH_4^+ ion) or the equilibrium constant K_b:

$$A + H_2O \rightleftarrows AH^+ + {}^-OH \qquad pK_b = pK_w - pK_a$$

where $pK_w = pK$ of water, i.e., about 16.

(A) The Hammett Acidity Function

The pH scale, which is a measure of acidity in dilute aqueous solutions, cannot be used to characterize the acidity of concentrated acids for the same reason that the concentrations in equations for chemical equilibria cannot be employed for the characterization of concentrated and non-aqueous solutions and must be replaced in this case by activities. Substitution of activities for concentrations enables one to extend the measure of acidity to concentrated and non-aqueous solutions. In this generalization, the **Hammett acidity function** H_0 is an extension of the pH scale for concentrated acids. This generalization, which was introduced by Hammett, is described below.

If an electrically neutral base B (an amine, any oxygen-containing organic compound, etc.) is introduced into an acid HX, the following equilibrium reaction will take place:

$$B + HX \rightleftarrows BH^+ + X^-$$

The cation BH^+ of the salt of base B dissociates according to the equation

$$BH^+ \rightleftarrows B + H^+$$

and the relevant dissociation constant K_a, which allows one to judge about the strength of base B, will be defined thus:

$$K_a = \frac{a_{H^+} a_B}{a_{BH^+}} = \frac{a_{H^+} \gamma_B [B]}{\gamma_{BH^+} [BH^+]}$$

where a with the corresponding subscripts are activities; γ with the subscripts are activity coefficients, and the expressions in square brackets are concentrations.

Let us designate the expression

$$\frac{a_{H^+}\gamma_B}{\gamma_{BH^+}}$$

by h_0; then

$$h_0 = K_a \frac{[BH^+]}{[B]}$$

The acidity function H_0 is defined as the negative common logarithm of h_0, i.e., $H_0 = -\log h_0$, and hence

$$H_0 = pK_a + \log \frac{[B]}{[BH^+]}$$

For dilute aqueous solutions of acids the activity coefficients are practically equal to unity and $h_0 = a_{H^+}$, and $H_0 = pK_a$. But in solutions of concentrated acids, for which the activity coefficients are different from unity and vary with concentration, H_0 serves as a measure of acidity and, as stated above, is an extension of the pK_a scale to the side of concentrated acids.

Reasoning just as for base B, we shall obtain analogous expressions for base B′ which, instead of the quantities [B], $[BH^+]$, γ_B and γ_{BH^+}, will contain [B′], $[B'H^+]$, $\gamma_{B'}$ and $\gamma_{B'H^+}$, and the dissociation constant of the conjugate acid $B'H^+$ will be equal to K'_a. Then

$$pK_a - pK'_a = \log \frac{[BH^+]}{[B]} - \log \frac{[B'H^+]}{[B']} + \log \frac{\gamma_{BH^+}\gamma_{B'}}{\gamma_B \gamma_{B'H^+}}$$

If

$$\log \frac{\gamma_{BH^+}\gamma_{B'}}{\gamma_B \gamma_{B'H^+}} = 0$$

or, what amounts to the same thing,

$$\log \frac{\gamma_{BH^+}}{\gamma_B} - \log \frac{\gamma_{B'H^+}}{\gamma_{B'}} = 0$$

then

$$\log \frac{\gamma_{BH^+}}{\gamma_B} = \log \frac{\gamma_{B'H^+}}{\gamma_{B'}} \quad \text{and} \quad pK_a - pK'_a = \log \frac{[BH^+]}{[B]} - \log \frac{[B'H^+]}{[B']}$$

For a wide range of weak bases in high-dielectric-constant solvents the equalities given above are fulfilled and, as shown above, the acidity function may be expressed as follows:

$$H_0 = pK_a + \log \frac{B}{[BH^+]}$$

The acidity function H_0 is determined in practice by using indicators with known pK_a (these data are available from appropriate

tables), the light absorption of whose conjugate acid BH^+ is sharply different from that of base B; the concentrations [B] and $[BH^+]$ are measured colorimetrically or spectrophotometrically.

From the last equation it follows that $H_0 = pK_a$ if $[B]/[BH^+] = 1$, i.e., if 50 per cent of the total amount of base B has captured a proton and is in the form of BH^+.

Since each indicator is applicable only in a narrow range of acidity, one has to make use of a number of indicators. As an example, we give the values of pK_a for a number of conjugate acids of weak bases used as indicators for determination of H_0:

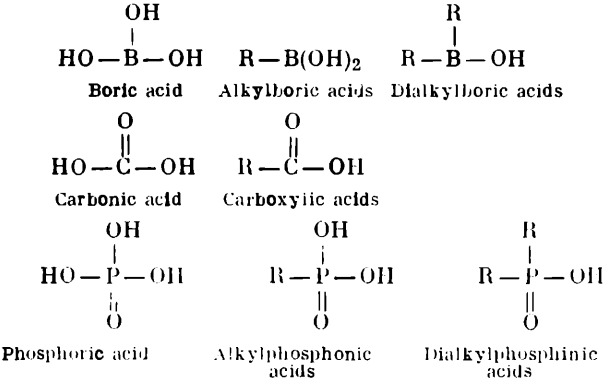
Base	pK_a	Base	pK_a
p-Nitroaniline	+1.11	Benzalacetophenone	−5.61
o-Nitroaniline	−0.13	*p*-Benzoylbiphenyl	−6.19
p-Nitrodiphenylamine	−2.38	Benzoic acid	−7.26
p-Nitroazobenzene	−3.35	Anthraquinone	−8.15
2,4-Dinitroaniline	−4.38	2,4,6-Trinitroaniline	−9.29

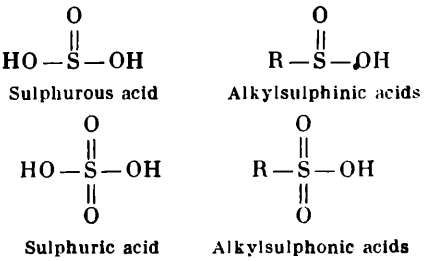
The values of H_0 for solutions of sulphuric acid of different concentration are as follows:

H_2SO_4, %	H_0	H_2SO_4, %	H_0
5	+0.24	60	−4.32
10	−0.16	70	−5.54
20	−0.89	80	−6.82
30	−1.54	90	−8.17
40	−2.28	95	−8.74
50	−3.23	100	−10.60

Organic acids (in the classical sense) contain, in their hydrocarbon chain, various functional groups which are the residues of inorganic polybasic acids or carbonic acid and which have retained at least one acidic hydrogen atom:

Inorganic prototype *Organic acids*



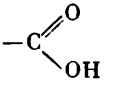


The acid esters of mineral acids considered on page 144 belong to the same category.

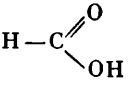
2.9. Carboxylic Acids

A. Saturated Monobasic Acids

This section is concerned with acids whose acidic properties are due to the presence of the *carboxyl* functional group



The homologous series of saturated monobasic acids has the general formula $C_nH_{2n}O_2$; the first member of this series is **formic acid**



The "common" or "trivial" names of the acids of this series—formic, acetic, propionic, butyric, etc. (Table 2.13)—have become so firmly entrenched in chemical literature and are applied to so many of the derivatives of the acids (salts, esters), whose names are derived from the corresponding Latin roots (formate, acetate, propionate, butyrate), that they are used everywhere. The names of carboxylic acids recommended by the Geneva nomenclature are derived from the corresponding names of saturated hydrocarbons by changing the final *-e* of the hydrocarbon name to *-oic* and add ng *acid* as a separate word; for example, methanoic acid for formic acid, ethanoic acid for acetic acid, etc. There is, however, still another system of nomenclature, very convenient in many cases, which must not be confused with the Geneva nomenclature. According to this system, a carboxylic acid is formally regarded as a product of replacement

TABLE 2.13. Saturated

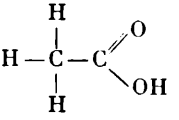
Formula	Name		
	trivial	Geneva	carboxylic system
$H-COOH$	Formic	Methanoic	—
CH_3-COOH	Acetic	Ethanoic	Methanecarboxylic
CH_3-CH_2-COOH	Propionic	Propanoic	Ethanecarboxylic
$CH_3-CH_2-CH_2-COOH$	Butyric	Butanoic	1-Propanecarboxylic
$CH_3-CH(CH_3)-COOH$	Isobutyric	2-Methylpropanoic	2-Propanecarboxylic
$CH_3-CH_2-CH_2-CH_2-COOH$	Valeric	Pentanoic	1-Butanecarboxylic
$CH_3-CH(CH_3)-CH_2-COOH$	Isovaleric	3-Methylbutanoic	1-Isobutanecarboxylic
$CH_3-(CH_2)_4-COOH$	Caproic	Hexanoic	1-Pentanecarboxylic
$CH_3-(CH_2)_5-COOH$	Enanthic	Heptoic	1-Hexanecarboxylic
$CH_3-(CH_2)_6-COOH$	Caprylic	Octanoic	1-Heptanecarboxylic
$CH_3-(CH_2)_7-COOH$	Pelargonic	Nonanoic	1-Octanecarboxylic
$CH_3-(CH_2)_{14}-COOH$	Palmitic	Hexadecanoic	1-Pentadecanecarboxylic
$CH_3-(CH_2)_{15}-COOH$	Margaric	Heptadecanoic	1-Hexadecanecarboxylic
$CH_3-(CH_2)_{16}-COOH$	Stearic	Octanedecanoic	1-Heptadecanecarboxylic
$CH_3-(CH_2)_{24}-COOH$	Cerotic	Hexacosanoic	Pentacosanecarboxylic

* This table does not cover all isomers, and only selected homologues are given.

Monobasic Acids*

m. p., °C	b. p., °C	Density d_4^{20}	Dissociation constant at 25°C, K_a	pK_a (at 25°C)
8.40	100.7	1.220	1.77×10^{-4} (at 20°C)	3.75 (at 20°C)
16.6	118.1	1.049	1.76×10^{-5}	4.75
—22.0	141.1	0.992	1.34×10^{-5}	4.87
—7.9	163.5 (at 757 mm Hg)	0.9587	1.54×10^{-5} (at 20°C)	4.81
—47.0	154.4	0.949	1.44×10^{-5} (at 18°C)	4.84
-59; —34.5	187.0	0.942	1.51×10^{-5} (at 18°C)	4.82
—37.6	176.7	0.937 (d_4^{15})	1.70×10^{-5}	4.77
1.5 to —2.0	205	0.929	1.31×10^{-5}	4.88
—10.0	223.5	0.918	1.28×10^{-5}	4.89
+16.0	237.5	0.910	1.28×10^{-5}	4.89
12.0	254	0.9055	—	—
64.0	271 (at 100 mm Hg) 339-356 (decomp.)	0.8530 (at 62°C)	—	—
60.6	227 (at 100 mm Hg)	0.8578 (d_4^{60})	—	—
69.4	291 (at 100 mm Hg)	0.847 (at 69°C)	—	—
87.7	Decomposes	0.8360 (at 79°C)	—	—

of the hydrogen atom of a hydrocarbon by a carboxyl group and, accordingly, acetic acid, for example,



is called methanecarboxylic and not ethanoic acid.

The functional group of carboxylic acids, the **carboxyl group**—COOH, is a combination of a carbonyl (C=O) and a hydroxyl group. This is confirmed by a number of reactions that have already been considered.

For instance, the action of phosphorus pentachloride on an acid leads to an ordinary replacement of the hydroxyl group by a chlorine atom and results in the formation of an acid chloride:

$$R-\underset{\underset{O}{\|}}{C}-OH + PCl_5 \longrightarrow R-\underset{\underset{O}{\|}}{C}-Cl + POCl_3 + HCl$$

With the aid of the Rosenmund reaction (see page 174) this chlorine atom can be substituted by hydrogen and the structure of the acid reduced to the structure of the corresponding aldehyde:

$$R-\underset{\underset{O}{\|}}{C}-Cl + H_2 \xrightarrow{Pd} R-\underset{\underset{O}{\|}}{C}-H + HCl$$

The fact that the parent compound (the acid) can be reformed through the reverse reaction—the oxidation of the aldehyde—is very important:

$$R-\underset{\underset{O}{\|}}{C}-H + O \longrightarrow R-\underset{\underset{O}{\|}}{C}-OH$$

Since the above reactions involve only the hydroxyl of the acid, it follows that the acid had the same carbonyl group that is retained in the aldehyde.

Carboxylic acids give rise to numerous functional derivatives which contain a modified carboxyl group. Such derivatives result from the replacement either of the hydrogen of the carboxyl group (as in salts) or of the entire hydroxyl (as in an acid chloride), or else from the replacement of the carbonyl oxygen. All these derivatives will be considered later in the text. Though the carboxyl group is a group consisting of a hydroxyl and a carbonyl group, its properties sharply differ from the properties of the hydroxyl group of alcohols and the carbonyl group of aldehydes and ketones. Two principal differences can be noted:

1. The carboxyl group is the bearer of acidic properties and the dissociation of carboxylic acids in water is expressed by the equation:

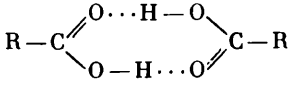
$$R-\underset{\underset{O}{\|}}{C}-OH + H_2O \rightleftharpoons RCOO^- + H_3O^+$$

The dissociation constants (see Table 2.13) of saturated monobasic acids (monocarboxylic acids) in aqueous solution at 25°C vary from 1.7×10^{-4} (formic acid) to about 1.3×10^{-5}. As compared with strong mineral acids they are weak acids, but their dissociation constants are nevertheless higher than the dissociation constant of water, not to mention those of alcohols.

2. The carbonyl group in the carboxyl is inert. It is incapable of entering into any of the reactions characteristic of the carbonyl group of aldehydes and ketones, except for reactions with organomagnesium compounds.

All these facts are accounted for by the phenomenon of mesomerism which will be discussed later (see pages 236 and 318 *et seq.*).

Like all hydroxyl compounds, carboxylic acids are associated liquids and are monomeric only in the vapour state and in aqueous solutions. But, in contrast to alcohols, their association is strictly regular—they form dimers in which two molecules of the acid are linked to each other via hydrogen bonding, the protons of the hydrogen bond being at different distances from its "own" (1 Å) and "foreign" (1.7 Å) oxygen atom:



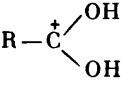
The dimer in the vapour state decomposes into monomers.

Being acids with respect to bases (including water), carboxylic acids are at the same time bases, though very weak, in relation to concentrated strong acids. The proton of strong acids is captured by carboxylic acids:

$$R-\underset{\underset{O}{\|}}{C}-OH + H_2SO_4 \rightleftharpoons R-\overset{+}{C}\begin{matrix}OH\\OH\end{matrix} + HSO_4^-$$

Conjugate acid

The value of pK_a for the acid conjugate with respect to acetic acid,



amounts to 6.1; $K_a = 10^{-6.1}$

The physical properties and names of saturated carboxylic acids—the homologues of formic acid—are listed in Table 2.13.

(a) *Preparation of Carboxylic Acids*

1. **Methods based on oxidation.** It has already been pointed out in considering the reactions of alkanes that the action of oxygen on alkanes (C_nH_{2n+2}) at 100°C in the presence of manganese salts as catalysts (the salt taken is usually $KMnO_4$ which is reduced in the process) leads to the formation of a mixture of acids of the general formula $C_mH_{2m+1}COOH$, which are formed as a result of the rupture of the chain caused by the oxidation of various methylenic linkages.

Ketones are oxidized, according to A. N. Popov (page 182), by strong oxidizing agents ($KMnO_4$) to a mixture of carboxylic acids.

Aldehydes are easily oxidized by an ammoniacal solution of silver oxide, complex compounds of divalent copper in alkaline medium, say, Fehling's solution (an alkaline solution of cuprous hydroxide in sodium tartrate) and by more powerful oxidants to acids with the same number of carbon atoms:

$$R-\underset{\underset{O}{\|}}{C}-H \xrightarrow{O} R-\underset{\underset{O}{\|}}{C}-OH$$

Primary alcohols are oxidized smoothly via the aldehyde stage (or directly) to acids having the same number of carbon atoms:

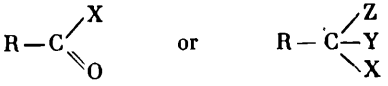
$$R-CH_2OH \xrightarrow{O} R-\underset{\underset{O}{\|}}{C}-H \xrightarrow{O} R-\underset{\underset{O}{\|}}{C}-OH$$

2O

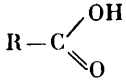
This reaction is of specific importance in the case of ethanol. Wine, a weak aqueous solution of alcohol which also contains the required nutrient substances, is oxidized by atmospheric oxygen during the life activity of many bacteria and fungi. This method has long been used to prepare vinegar (from wine)—dilute aqueous solutions of acetic acid, which are used as a table vinegar. On filtration of wine, with access of air, through a layer of beech shavings moistened with acetic bacteria there takes place a single-pass exothermal oxidation of wine to vinegar. Pure solutions of ethanol, in contrast to wine of the same concentration, do not become soured because they contain no nutrient substances necessary for the bacteria.

The oxidation of any primary alcohol to an acid can be effected by means of a powerful oxidizing agent such as chromic acid.

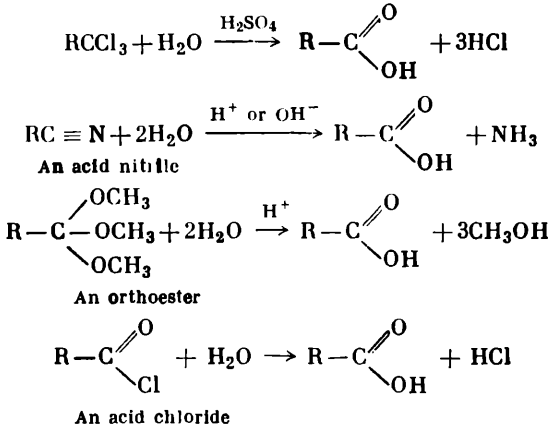
2. **Methods based on hydrolysis.** Any compound of the type



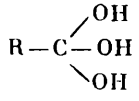
where X, Y, and Z are halogen, oxygen or nitrogen atoms (in the last two cases, the atoms are bound to hydrogen or to any group of atoms), forms on hydrolysis the acid



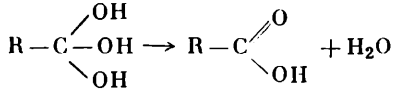
This can be illustrated by the following examples:



The first three reactions might be expected, as a result of hydrolysis, to lead to the formation of the compound



(the so-called *orthoacid*). But even two hydroxyls are held by one carbon atom only in exclusive cases (see page 176), this being impossible with three hydroxyls. As the result of the removal of water from the orthoacid, a carboxylic acid is formed:



It is especially necessary to throw light on the relations of formic acid, which are disclosed by hydrolysis reactions:

$$HCCl_3 + 4KOH \longrightarrow H-\underset{\underset{O}{\|}}{C}-OK + 3KCl + H_2O$$

$$HCN + 2H_2O \xrightarrow{H^+} H-\underset{\underset{O}{\|}}{C}-OH + NH_3$$

Hydrocyanic acid is thus the nitrile of formic acid.

The hydrolysis of acid nitriles is of great importance as a method of synthesis of carboxylic acids since nitriles are easily obtained by alkylation of the salts of hydrocyanic acid:

$$RCl + NaCN \longrightarrow RCN + NaCl$$

and their hydrolysis gives acids containing one carbon atom more than the parent alkyl halide:

$$RCN + 2H_2O \longrightarrow RCOOH + NH_3$$

This route of synthesis may therefore be also applied to the following group of methods for preparing acids.

3. **Methods based on extension of the carbon chain.** The interaction of carbon monoxide at a pressure of 6-8 kg/cm² and at 120-130°C with caustic alkali or with metal alkoxides gives a salt of formic acid in the first case and its homologues in the second:

$$HONa + CO \longrightarrow H-\underset{\underset{O}{\|}}{C}-ONa$$

$$RONa + CO \longrightarrow R-\underset{\underset{O}{\|}}{C}-ONa$$

Only the first reaction is of industrial importance since formic acid is now produced exclusively by this reaction.

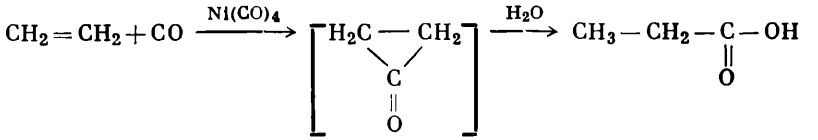
The action of carbon dioxide on organometallic compounds of alkali metals, magnesium and aluminium gives the salts of acids containing one carbon atom more than the alkyl groups of the organometallic compounds taken:

$$RLi + CO_2 \longrightarrow R-\underset{\underset{O}{\|}}{C}-OLi \xrightarrow{HCl} R-\underset{\underset{O}{\|}}{C}-OH + LiCl$$

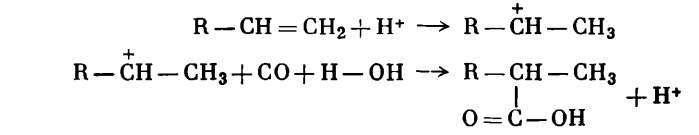
$$RMgCl + CO_2 \longrightarrow R-\underset{\underset{O}{\|}}{C}-OMgCl \xrightarrow{HCl} R-\underset{\underset{O}{\|}}{C}-OH + MgCl_2$$

This is one of the most important laboratory methods for synthesizing carboxylic acids.

The synthesis of acids (beginning with propionic) based on the action of carbon monoxide and water on olefins in the presence of nickel carbonyl as a catalyst (the Reppe synthesis) has become industrially important:

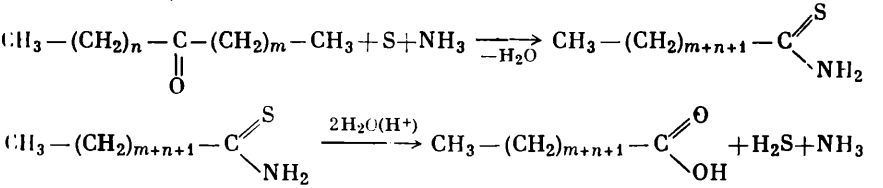


In 1958, Haaf and Koch developed a method for preparing carboxylic acids by the action of carbon monoxide on olefins in a concentrated solution of sulphuric acid. The reaction consists in the alkylation of the carbon monoxide formed from olefin and hydrogen ion with alkyl cation (Markovnikov's rule, see page 336):

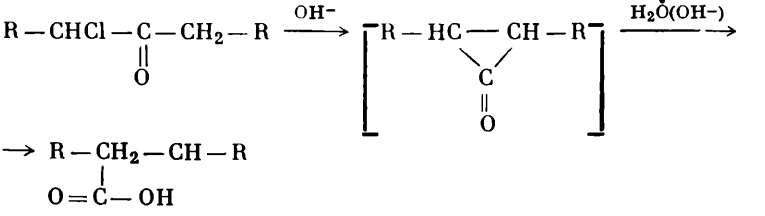


In these reactions, instead of carbon monoxide, use may be made of formic acid which forms carbon monoxide with sulphuric acid, and fluorosulphonic acid or boron trifluorate hydrate, $H^+[HOBF_3]^-$, may be used instead of sulphuric acid.

4. **Methods involving no change of the carbon-chain length.** Mention may be made of the notable **Willgerodt reaction**—the conversion of ketones to acids having the same number of carbon atoms, the mechanism of which has not yet been clearly understood. A ketone with its carbonyl group being in any position (not only in the α-position) gives an acid under the action of sulphur and ammonia (or an amine) followed by hydrolysis:



The rearrangement of α-chloroketones to acids under the influence of alkali (A. E. Favorsky) is increasing in importance:



(b) *Chemical Properties of Carboxylic Acids*

The most characteristic and important properties of carboxylic acids are associated with their conversion into functional derivatives. The corresponding reactions will be considered in a special section devoted to the functional derivatives of carboxylic acids (see Sec. 2.10). At this point we shall discuss other chemical conversions of the acids.

1. The pyrolysis of the alkali metal salts of the acids mixed with caustic alkali involves the decarboxylation and formation of hydrocarbons:

$$CH_3-\underset{\underset{O}{\|}}{C}-ONa+NaOH \longrightarrow CH_4+Na_2CO_3$$

$$C_2H_5-\underset{\underset{O}{\|}}{C}-ONa+NaOH \longrightarrow C_2H_6+Na_2CO_3$$

2. The pyrolysis of the calcium salts of the acids in the absence of alkali involves the formation of a ketone with partial decarboxylation (the Piria reaction):

$$\left(CH_3-\underset{\underset{O}{\|}}{C}-O\right)_2 Ca \longrightarrow CH_3-\underset{\underset{O}{\|}}{C}-CH_3+CaCO_3$$

3. The electrolysis of sodium salts of the acids on the anode also involves the decarboxylation of the acid anion, and the radicals formed are coupled into a hydrocarbon (the Kolbe reaction):

$$CH_3-\underset{\underset{O}{\|}}{C}-O^- - e \longrightarrow CH_3-\underset{\underset{O}{\|}}{C}-O\cdot \longrightarrow CH_3\cdot + CO_2$$

$$2CH_3\cdot \longrightarrow C_2H_6$$

4. Some of the functional derivatives of the acids can be reduced to the corresponding aldehydes and primary alcohols. The simplest way for reducing an acid to an aldehyde is the Rosenmund reaction (see page 174). The most widespread method of conversion of an acid to an alcohol (the Bouveault reaction) is the reduction of an ester of a carboxylic acid with pure (free of potassium, V. V. Loginov) metallic sodium in absolute ethyl alcohol:

$$R-\underset{\underset{O}{\|}}{C}-OC_2H_5+3C_2H_5OH+4Na \longrightarrow R-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-OH+4C_2H_5ONa$$

5. Like alkanes, carboxylic acids undergo chlorination and bromination upon irradiation or in the presence of peroxide catalysts, i.e., by a free-radical mechanism. Substitution takes place in different positions; in acids with a long unbranched chain, it occurs

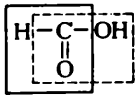
chiefly at the β-position. Acid halides are brominated only at the α-position. According to the Hell-Volhard-Zelinsky method, the bromination is carried out in the presence of phosphorus tribromide or red phosphorus. When phosphorus tribromide (or pentabromide) is used, an acid bromide is formed, which is then brominated:

$$R-CH_2-\underset{\underset{O}{\|}}{C}-Br \xrightarrow[-HBr]{+Br_2(PBr_5)} R-\underset{\underset{Br}{|}}{CH}-\underset{\underset{O}{\|}}{C}-Br \xrightarrow[-HBr]{+H_2O} R-\underset{\underset{Br}{|}}{CH}-\underset{\underset{O}{\|}}{C}-OH$$

6. Acids can be oxidized to SeO_2 at the α-methylene link to α-keto acids:

$$R-CH_2-\underset{\underset{O}{\|}}{C}-OH + SeO_2 \longrightarrow R-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-OH + H_2O + Se$$

Formic acid—the first member of the series—occupies a special place among its homologues. Even its structural formula



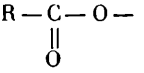
shows that it has a carboxyl (marked by a dotted line) and an aldehyde group (marked by a heavy line). As has already been pointed out, the carbonyl group adjacent to the hydroxyl loses most of its typical properties (see page 208), say, its ability to take part in addition and substitution reactions, particularly in polymerization and condensation. This "aldehyde" group, however, retains its ability to be oxidized even by weak oxidizing agents such as $Ag(NH_3)_2OH$, Fehling's solution, and others:

$$H-\underset{\underset{O}{\|}}{C}-OH + O \longrightarrow HO-\underset{\underset{O}{\|}}{C}-OH \longrightarrow CO_2 + H_2O$$

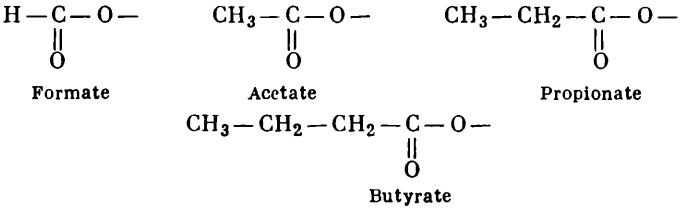
2.10. Functional Derivatives of Carboxylic Acids

Functional derivatives of carboxylic acids are formed by substitution in the carboxyl group. This may involve the replacement of an acid hydrogen atom (by a metal or alkyl), of a hydroxyl (by a halogen, a NH_2 group, etc.), the carbonyl oxygen and also both the hydroxyl group and the carbonyl oxygen.

In the first case (when the acid hydrogen is replaced) the acid residue has the formula

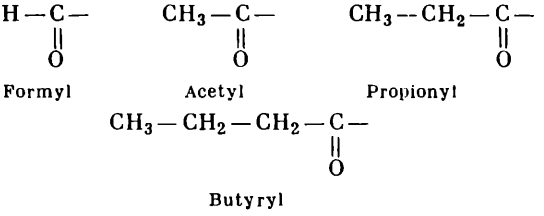


and is called the **carbalkoxy group** or sometimes the **acyloxy** group; examples are:



In the second case (replacement of the hydroxyl group) the residue

is called the **acyl group.** The derivatives are named after the corresponding acid by adding the termination *-yl* to a suitable contraction of the latter, e.g.



A. Salts of Carboxylic Acids

The neutralization of carboxylic acids with alkali leads to the formation of salts. In aqueous solution the salts of alkali metals are strongly hydrolysed. The hydrolytic equilibrium constant is equal to the ratio of the dissociation constant of water to that of the acid.

The sodium salts of higher fatty acids (for example, stearic acid, $C_{17}H_{35}COOH$) obtained by the action of alkali on vegetable and animal fats and oils (this process is carried out in soap manufacture) are known as **soaps.** Hence the name of **saponification** for the reaction of hydrolysis of esters.

Soaps have long been known in the home and in industry as the most **surface-active substances** (sometimes called **surfactants**). The cleansing action of soaps and, in particular, of detergents, consists

in the following. Salts of carboxylic acids dissociate in aqueous solution into ions:

$$R-\underset{\underset{O}{\|}}{C}-ONa \rightleftarrows R-\underset{\underset{O}{\|}}{C}-O^- + Na^+$$

If the carboxylate anion is small (R = H, CH_3, C_2H_5, C_3H_7), it dissolves well in water, though this takes place due to the solvation of only the carboxyl part of the anion. But if R is a long hydrocarbon (paraffin) chain, say, $C_{15}H_{31}$ or $C_{17}H_{35}$, then such a residue, like the hydrocarbons themselves, is insoluble in water (hydrophobic), whereas the carboxyl portion of the anion retains its hydrophilic character. Owing to this difference, the soap molecules become concentrated on the surface of water, covering the latter with a layer in which the carboxylate ions are attracted to the water and the paraffin chains to the surface. If a layer of a hydrocarbon or an oil is poured into water, the paraffin radicals will dissolve in it and all the soap molecules will tend to reside on the interface. This effects a decrease in interfacial tension, which is a measure of the forces tending to reduce the surface. The interface will increase, this being achieved only through the distribution of one liquid in the other in droplets (an emulsion is formed). When soap is added to a mixture of water and a water-insoluble organic liquid, stable emulsions are formed, which is widely made use of in the various sections of national economy. This method is used to prepare, for example, emulsions of higher hydrocarbons of petroleum fractions to combat plant-killers. Since the dirt on the body and underwear consists basically of fat or grease particles insoluble in water, it cannot be washed away with water, but when the fat is emulsified in the soap solution it is carried away with water.

In more concentrated soap solutions, all the molecules cannot be lodged in the surface layer and are partially distributed also in the bulk. In this case, the hydrophobic nature of the radicals makes them pack together into clusters, each consisting of many units; a colloidal solution results, which scatters the ray of light passing throught it (the Tyndall effect). It is from such colloidal solutions that common salt "salts out" hard soap. It is for this reason that ordinary soaps cannot be used for washing in sea water and resort has to be made to other surface-active agents (for example, salts of sulphonic acids).

The calcium salts of higher fatty acids are slightly soluble in water, and therefore the soap gives a precipitate in hard water and fails to fulfill its function.

The potassium salts of higher fatty acids are well soluble in water and form so-called green liquid soaps. These are concentrated aqueous solutions (hence liquid) of potassium salts made green.

Numerous salts of lower and higher fatty acids with heavy metals are known. In most cases, they are not so prominently ionic as the salts of alkali metals, and form a polarized but covalent bond with the metal. For example, the acetate of divalent copper is coloured not dark blue, which is typical of the ion of this metal, but intense blue-green.

Manganese and some other salts of higher fatty acids are used as initiators of oxidation and polymerization processes (for example, in the drying process for producing drying oils) and are called **siccatives.**

B. Esters of Carboxylic Acids

The reactions used to prepare esters are as follows.

1. Esterification. An alcohol and a carboxylic acid react together to form an ester:

$$R-\underset{\underset{O}{\|}}{C}-OH + R'OH \rightleftarrows R-\underset{\underset{O}{\|}}{C}-OR' + H_2O$$

The reaction is catalysed by hydrogen ions. Experiments with an acid labelled with ^{18}O show that the acid hydroxyl is isolated in the form of water, $H_2^{18}O$, and the alcohol gives up only its hydrogen. The esterification reaction is reversible and the hydrogen ion also catalyses the reverse reaction—the hydrolysis of the ester.

The role of the hydrogen ion can be visualized as follows:

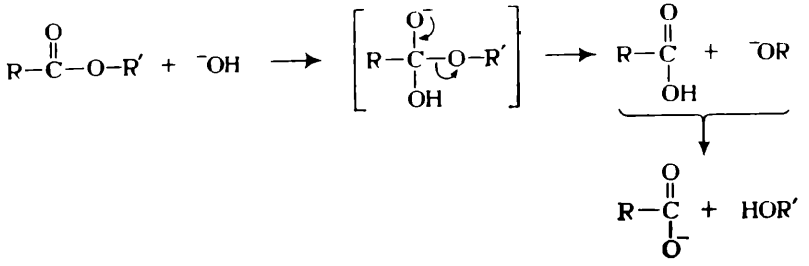
$$R-\overset{\overset{O}{\|}}{C}-O-R' + H_2O + H^+ \rightleftarrows \left[R-\overset{\overset{O}{\|}}{C}(-\overset{H^+}{O}-R')(-\overset{H}{\underset{H}{O}}) \right] \rightleftarrows R-\overset{\overset{O}{\|}}{C}(-\overset{H}{\underset{H}{O}}) + O-R' + H^+$$

Enclosed in square brackets is the reaction complex (the transition state). The curved arrows show the direction of the electron shift which begins in the reaction complex and ends in the final products. This mechanism has been suggested by the results of the hydrolysis of an ester labelled with the heavy oxygen isotope (^{18}O) in the ester group:

$$R-\underset{\underset{O}{\|}}{C}-{}^{18}O-R' \xrightarrow{H_2O} R-\underset{\underset{O}{\|}}{C}-OH + R'-{}^{18}O-H$$

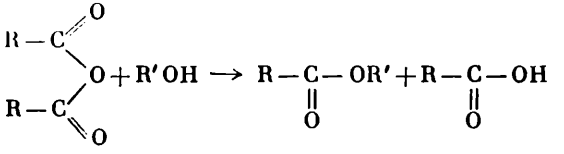
The role of the hydrogen ion in esterification reactions can be ascertained by reading the equation from right to left.

The hydrolysis of an ester is also catalysed by hydroxyl ions:

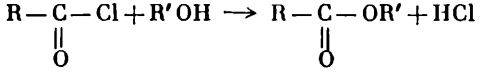


The rate of an esterification reaction is the highest for primary alcohols. The esters of tertiary alcohols and carboxylic acids cannot be obtained by direct esterification.

2. **Interaction of acid anhydrides with alcohols.** A generalized equation for the reaction between an acid anhydride (page 228) and an alcohol is



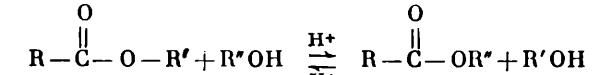
3. **Interaction of acid halides with alcohols.** The reaction of an acid halide (page 225) with an alcohol proceeds according to the scheme



The physical properties of certain esters are listed in Table 2.14.

The esters of lower carboxylic acids and the simplest alcohols are liquids with a refreshing fruity odour. They are used as artificial flavorings for beverages. Many of the esters (ethyl acetate, butyl acetate, isoamyl or amyl acetate) are widely used in industry as solvents, especially for varnishes and lacquers.

As to the chemical properties of carboxylic esters, mention should be made of their tendency to undergo transesterification with alcohols in acid solution:

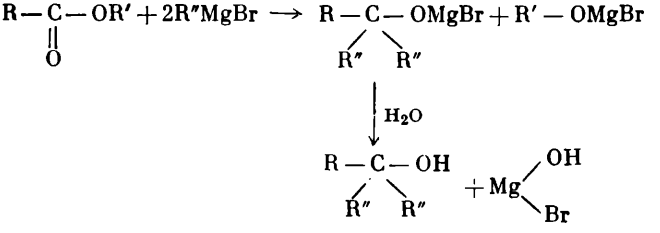


The mechanism of this reaction is evidently the same as that of acid hydrolysis.

TABLE 2.14. **The Esters of Formic Acid Homologues**

Formula	R	Name	m.p., °C	b.p., °C	Density d_4^{20}
HCOOR	CH_3	Methyl formate	—99.0	31.5	0.975
	C_2H_5	Ethyl formate	—80.5	54.3	0.917
CH_3COOR	CH_3	Methyl acetate	—98.1	57.1	0.924
	C_2H_5	Ethyl acetate	—83.6	77.1	0.901
	n-C_3H_7	*n*-Propyl acetate	—92.5	101.6	0.887 (d_4^{25})
	n-C_4H_9	*n*-Butyl acetate	—76.8	126.5	0.882 (d_4^{25})
	iso-C_5H_{11}	Isoamyl acetate	—78.5	142.5	0.870
C_2H_5COOR	CH_3	Methyl propionate	—87.5	79.9	0.915
	C_2H_5	Ethyl propionate	—73.9	99.1	0.888
C_3H_7COOR	CH_3	Methyl butyrate	< —95.0	102.3	0.898
	C_2H_5	Ethyl butyrate	—93.3	121.3	0.879
n-C_4H_9COOR	CH_3	Methyl valerate	—91.0	127.3	0.910 (at 0°C)
	C_2H_5	Ethyl valerate	—91.2	146.0	0.874

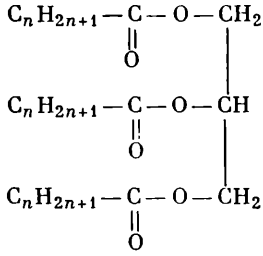
With Grignard reagents, esters form tertiary alcohols:



Fats (solids) and **oils** (liquids)* are esters formed from glycerol and the homologues of acetic acid, beginning with butyric and up to stearic (and upwards). Natural fats and oils contain acids only with

* The fats are solid at room temperature, while the oils are liquid. This distinction, however, is somewhat arbitrary since what could be regarded in this country as a fat might well be a flowing oil in the tropics.—*Tr.*

an even number of carbon atoms. Moreover, oils contain a higher percentage (than do the fats) of unsaturated fatty acids with the same number of carbon atoms, whose chains include one to three double bonds (page 414). The structure of saturated fats and oils is as follows:



where n is an odd number. One molecule of fat or oil may contain different acid residues.

The esters of glycerol are called **glycerides**. Ox tallow contains a large amount of the glyceride of stearic acid ($n = 17$, *tristearin*); mutton or human fats and also coconut oil are the glycerides of palmitic acid ($n = 15$, *tripalmitin*); cow butter (cream butter or boiled butter) contain, in addition to the glycerides indicated above, the glycerides of butyric acid and acids, intermediate between butyric acid and palmitic acid, having an even number of carbon atoms.

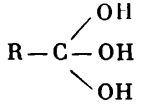
Liquid fats and drying oils will be considered in a section dealing with unsaturated acids.

Fats are hydrolysed with alkali for the manufacture of soaps. The solution (saponified) that has been subjected to hydrolysis is chilled, the entire glycerol ("glycerol soap") being retained in it. In another method, the solution is saturated with common salt (the process being called "salting out"); solid clots of soap are precipitated and the so-called grained soap is formed.

The hydrolysis of fats with superheated steam results in the formation of a water-insoluble mixture of fatty acids (in the form of a melt) and an aqueous solution of glycerol, which is concentrated by distilling off the water. The resulting mixture of higher fatty acids is known as stearine and was formerly used in the manufacture of candles.

C. Ortho Esters

The alkyl derivatives of non-existent ortho forms of carboxylic acids with the general formula



are called **ortho esters.** They are prepared in various ways.

1. Heating of 1,1,1-trichloroalkanes, $RCCl_3$, having no hydrogen atoms at the α-carbon, with a sodium alkoxide:

$$RCCl_3 + 3NaOR' \longrightarrow R-C(OR')_2(OR') + 3NaCl$$

This method is used to prepare an orthoformic ester from chloroform:

$$HCCl_3 + 3NaOCH_3 \longrightarrow H-C(OCH_3)_2(OCH_3)$$

If there are two hydrogen atoms at the α-carbon, then the action of the alkoxide brings about the splitting-off of HCl:

$$R-CH_2-CCl_3 + NaOR' \longrightarrow R-CH=CCl_2 + NaCl + R'OH$$

2. The action of hydrogen chloride and an excess of alcohol on acid nitriles:

$$R-C\equiv N \xrightarrow{HCl} R-C(Cl)=NH \xrightarrow{R'OH} R-C(OR')=NH \xrightarrow{2R'OH+HCl}$$

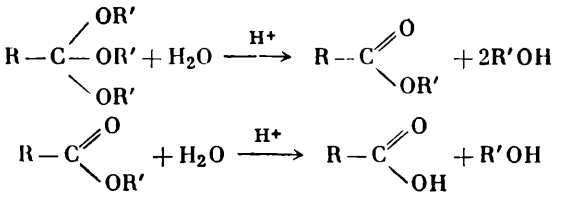
$$\longrightarrow R-C(OR')_2(OR') + NH_4Cl$$

The physical properties of some ortho esters are given in Table 2.15.

TABLE 2.15. **Esters of Orthocarboxylic Acids**

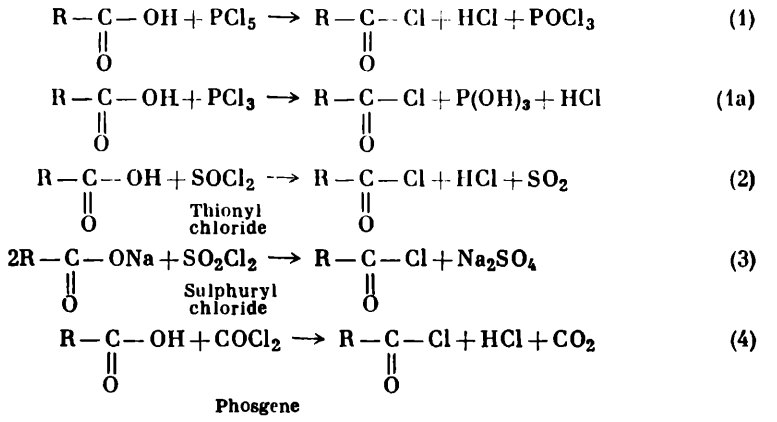
Formula	Name	m.p., °C	b.p., °C	Density d
$HC(OCH_3)_3$	Trimethyl orthoformate	—	105	0.974 (at 23°C)
$HC(OC_2H_5)_3$	Triethyl orthoformate	—76.1	145.9	0.897 (d_4^{19})
$CH_3C(OCH_3)_3$	Trimethyl orthoacetate	—	109	0.9437 (d_4^{25})
$CH_3C(OC_2H_5)_3$	Triethyl orthoacetate	—	142	0.885 (d_4^{25})
$C(OCH_3)_4$	Tetramethyl orthocarbonate	—5.5	114	1.0232 ($d_{18.5}^{18.5}$)
$C(OC_2H_5)_4$	Tetraethyl orthocarbonate	—	159	0.919 (d_4^{18})
$C(OC_3H_7)_4$	Tetrapropyl orthocarbonate	—	224.2	0.911 (at 8°C)

Ortho esters are hydrolysed by stages: an ester is formed first which then gives an acid and an alcohol:



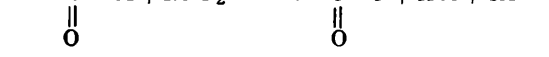
D. Acid Halides

The most important and thoroughly studied compounds of this class are acid chlorides. They are usually made from acids by one of the following reactions:



For laboratory syntheses, use is normally made of reactions (1), (2) and (1a); on an industrial scale, acid chlorides are prepared by reactions (3) and (4). Acid bromides are made by reactions of the (1a) type; slightly stable acid iodides are prepared in the same way.

Acid fluorides are synthesized by the exchange of the halogen in acid chlorides for fluorine through the action of KHF_2:

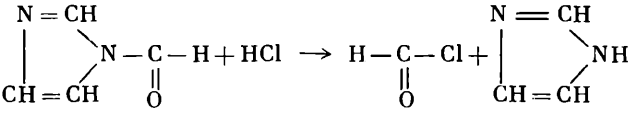


An acid fluoride of a lower-boiling acid can be made by dissolving KF or KHF_2 in that acid and by the action of an acid chloride of a higher-boiling acid on it. The exchange of the acid hydroxyl for the chlorine of the acid chloride proceeds smoothly:

This method was used to prepare formyl fluoride, HCOF, which was the first formic acid halide, though unstable (A. N. Nesmeyanov and E. I. Kahn). The other halides of formic acid decompose as they are formed:

$$H-\underset{\underset{O}{\|}}{C}-Cl \longrightarrow HCl + CO$$

It was only in 1963 that Staab reported the preparation of formyl chloride at —60°C by the action of hydrogen chloride in chloroform on formyl imidazole:

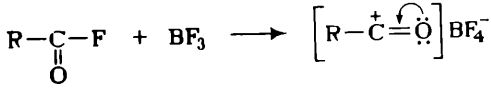


At —60°C formyl chloride exists in solution for several hours, but all attempts to isolate it have failed.

Table 2.16 gives the physical properties of some of the simplest acid halides.

The halogen in acid halides is extremely active (mobile), i.e., it readily enters into exchange reactions. In this respect, all the halogens exhibit almost the same behaviour. The factor responsible for the mobility of the halogens is the partial positive charge ($\delta+$) on the carbon attached with its three valencies to highly electronegative atoms (oxygen and chlorine) and hence the availability of the carbon atom for nucleophilic attack.

Acid fluorides react with BF_3, one of the strongest Lewis acids, which particularly strongly captures the fluoride ion, forming the stable complex anion BF_4^-. This results in the formation of solid salt-like substances (Zeele):



These substances have sharply pronounced acylating properties. It should be assumed that the unshared pair of electrons on the oxygen is partly drawn to the positively charged carbon in the cation, as a result of which the positive charge is distributed between carbon and oxygen.

The actual structure of the **acylium cation** may be represented with the aid of two extreme structures:

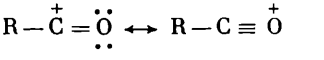


TABLE 2.16. Carboxylic Acid Halides

Formula	Name	m.p., °C	b.p., °C	Density d_4^{20}	Refractive index n_D^{20}
HCOF	Formyl fluoride	—	—26 (at 750 mm Hg)	1.60 (at —26°C)	—
CH_3COF	Acetyl fluoride	<-60	20.5	0.993	—
CH_3COCl	Acetyl chloride	—112	52	1.105	1.3897
CH_3COBr	Acetyl bromide	—96.5	76.7	1.663 (d_4^{16})	1.4537 (at 16°C)
CH_3COI	Acetyl iodide	—	106	2.067	1.5491
CH_3CH_2COCl	Propionyl chloride	—94	80	1.065	1.4051
$CH_3CH_2CH_2COCl$	*n*-Butyryl chloride	—89	102	1.028	1.4121
$(CH_3)_2CHCOCl$	Isobutyryl chloride	—90	92	1.017	1.4079
$CH_3CH_2CH_2CH_2COCl$	*n*-Valeryl chloride	—110	128	1.016 (at 15°C)	1.4155
$(CH_3)_2CHCH_2COCl$	Isovaleryl chloride	—	114.5	0.989	1.4149

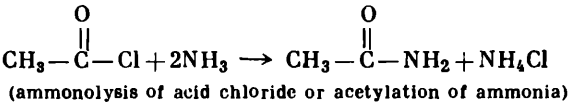
The reactions of acyl halides given below by way of examples proceed at a fast rate or even vigorously at room temperature. In these reactions, the acyl halide acylates the reactant molecule, i.e., introduces an acyl group into it in place of hydrogen:

$$CH_3-\overset{\overset{O}{\|}}{C}-Cl + H_2O \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-OH + HCl$$

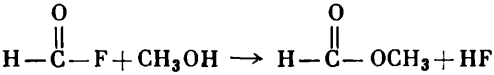
(hydrolysis of acid chloride or acetylation of water)

$$CH_3-\overset{\overset{O}{\|}}{C}-Cl + C_2H_5OH \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-OC_2H_5 + HCl$$

(alcoholysis of acid chloride or acetylation of ethanol)



(ammonolysis of acid chloride or acetylation of ammonia)

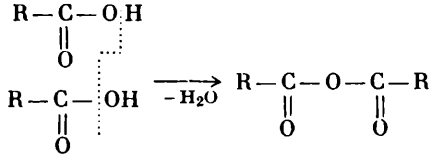


(alcoholysis of acid fluoride or formylation of methanol)

We shall encounter other examples of acylation reactions in the discussion of other functional derivatives of carboxylic acids.

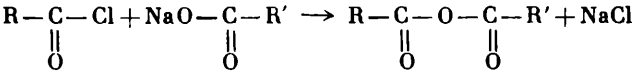
E. Acid Anhydrides

Acid anhydrides may be regarded as the products of dehydration of two molecules of a carboxylic acid:

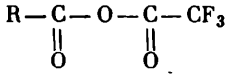


In the case of certain dibasic acids, such a reaction can be carried out by heating, but in the homologous series of acetic acid the anhydrides can be obtained only by dehydration with the aid of P_2O_5. The anhydride of formic acid does not exist at all.

Acid anhydrides are prepared by acylation of the salts of carboxylic acids with acid chlorides:



Here R and R′ may be either identical or different. In the latter case, mixed anhydrides of two acids are obtained. Of particularly great significance are the mixed anhydrides of trifluoroacetic acid:



which are the strongest acylating agents (they are used to introduce an acyl group).

The formerly employed industrial method of preparing acetic anhydride was based on the reaction of the salts of the acids with their acid chlorides. The acid chloride was not isolated; it was obtained directly in the reaction medium by the action of SO_2Cl_2 or $COCl_2$ on sodium acetate. The second molecule of sodium acetate gives acetic anhydride with the acetyl chloride formed.

The physical properties of certain acid anhydrides are presented in Table 2.17.

TABLE 2.17. Carboxylic Acid Anhydrides

Formula	Name	m.p., °C	b.p., °C	Density d_4^{20}	Refractive index n_D^{20}
$(CH_3CO)_2O$	Acetic	—73.1	140	1.087	1.3904
$(C_2H_5CO)_2O$	Propionic	—45	169.3	1.0336	1.4038
$(n\text{-}C_3H_7CO)_2O$	Butyric	—75.0	198; 201	0.9946	1.4070
$(n\text{-}C_4H_9CO)_2O$	Valeric	—56.1	215	0.9290	1.4171
$(C_5H_{11}CO)_2O$	Caproic	—40.6	243; 254	0.9279	1.4297
$(C_6H_{13}CO)_2O$	Enanthic	17	173 (at 15 mm Hg)	0.9320	1.4312
$(n\text{-}C_{17}H_{35}CO)_2O$	Stearic	71.5	—	0.8368 (d_4^{82})	1.4362 (at 80°C)

Acetic anhydride is a liquid which boils at 140°C and has extremely unpleasant, pungent odour, similar to that of acetic acid. Acetic anhydride has found extensive use in industry in the various acetylation processes (as a reagent for introducing acetyl groups into cellulose, phenols, aromatic amines, etc.). It is preferred to the corresponding acid chloride (acetyl chloride) whose boiling point is too low and which is highly reactive and is therefore less convenient in industrial conditions.

The modern method of preparing acetic anhydride, which is increasing in importance, is the action of ketene (Sec. 3.11) on anhydrous (glacial) acetic acid:

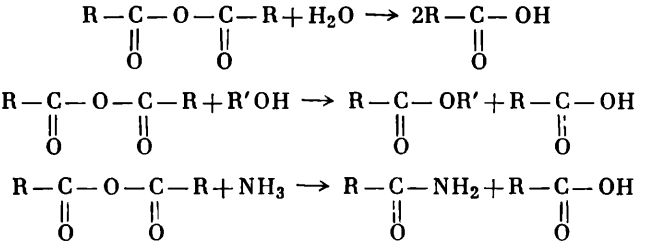
$$CH_3-\overset{\overset{O}{\|}}{C}-OH + \underset{\text{Ketene}}{CH_2=C=O} \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-CH_3$$

Ketene itself is an acid anhydride and can be obtained, for example, by the thermal decomposition (pyrolysis) of acetic acid:

$$CH_3-\overset{\overset{O}{\|}}{C}-OH \xrightarrow[-H_2O]{} CH_2=C=O$$

As seen from this reaction, ketene is itself an acetylating agent. In fact, it can be used instead of acetic anhydride or acetyl chloride in acetylation reactions, but the inconvenience of its use is that it is a gas, dimerizes rapidly and cannot therefore be preserved; the acetic anhydride made from it is free from these limitations.

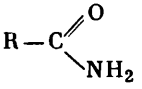
The acylation with anhydrides may be characterized by reactions analogous to those given above as examples of acylation with acid chlorides (hydrolysis, alcoholysis, ammonolysis):



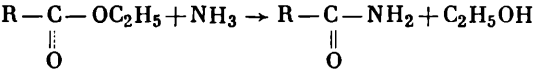
The use of the anhydride is disadvantageous because half of its molecule remains unacylated and returns in the form of the acid.

F. Acid Amides

We have just given the reaction of acylation of ammonia with an acid anhydride and also an analogous reaction with an acid chloride. The acylation products in both cases are acid amides of the general formula

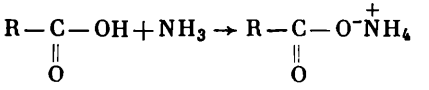


Ammonia can also be acylated by such a weak acylating agent as an ester:

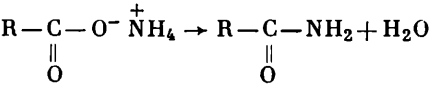


This reaction is called ammonolysis with respect to the ester.

When an acid is reacted with ammonia, an ammonium salt is naturally expected to form first:



which loses the elements of water on heating (dry distillation), being converted into an amide:



This is an important reaction and is used for industrial preparation of amides.

TABLE 2.15. Carboxylic Acid Amides

Formula	Name	m.p., °C	b.p., °C	Density d_4^{20}	Refractive index n_D	Solubility in water, g/100 ml
$HCONH_2$	Formamide	2.55	195 (at 10 mm Hg)	1.134	1.4453 (at 22.7°C)	Readily soluble
CH_3CONH_2	Acetamide	81	222	1.159	1.4274 (at 78.3°C)	97.5 (at 20°C)
$C_2H_5CONH_2$	Propionamide	79	213	1.042	1.4161 (at 108°C)	Soluble
n-$C_3H_7CONH_2$	n-Butyramide	116	216	1.032	1.4087 (at 130°C)	16.28 (at 15°C)
n-$C_4H_9CONH_2$	n-Valeramide	116	—	1.023	1.4183 (at 110°C)	Soluble
n-$C_5H_{11}CONH_2$	n-Capramide	101.0	255	0.999	1.4200 (at 110°C)	Dissolves very slightly
n-$C_{17}H_{35}CONH_2$	n-Stearamide	109	251 (at 12 mm Hg)	—	—	Insoluble
$(CH_3CO)_2NH$	Diacetamide	78	223.5	—	—	Soluble

The physical properties of selected amides are presented in Table 2.18. The lower amides are well soluble in water. The simplest amide is **formamide**, $HCONH_2$, the only one among the amides which is a liquid at room temperature and has a high dielectric constant. It is prepared by the action of carbon monoxide on ammonia in the presence of small amounts of sodium alkoxide:

$$CO + NH_3 \rightarrow H-\underset{\underset{O}{\|}}{C}-NH_2$$

The next member of this series is acetamide, CH_3CONH_2, which is a crystalline substance with a melting point of 81°C.

When alkylated ammonias—amines, say, CH_3NH_2 or $(CH_3)_2NH$—are acylated, alkyl and dialkyl amides are obtained:

$$R-\underset{\underset{O}{\|}}{C}-Cl + 2CH_3NH_2 \rightarrow R-\underset{\underset{O}{\|}}{C}-NHCH_3 + CH_3\overset{+}{N}H_3Cl^-$$

$$R-\underset{\underset{O}{\|}}{C}-Cl + 2(CH_3)_2NH \rightarrow R-\underset{\underset{O}{\|}}{C}-N(CH_3)_2 + (CH_3)_2\overset{+}{N}H_2Cl^-$$

Formamide and its dialkyl derivative—dimethylformamide, $HCON(CH_3)_2$—are used as industrial solvents. They are particularly applicable in the production of synthetic fibres. Dimethylformamide is an aprotic solvent (*aprotic* substances are those which are incapable of yielding or accepting a proton, i.e., substances which act neither as an acid nor as a base).

Amides are nearly devoid of the basic properties of ammonia and are practically neutral in aqueous medium. The conjugate acid of acetamide

$$CH_3-\underset{\underset{O}{\|}}{C}-\overset{+}{N}H_3$$

has a pK_a value of about 1.5 in aqueous solution.

When heated with an aqueous solution of acids or alkalis, amides are hydrolysed, forming an acid (or a salt) and ammonia:

$$R-\underset{\underset{O}{\|}}{C}-NH_2 + H_2O \rightarrow R-\underset{\underset{O}{\|}}{C}-O^-\overset{+}{N}H_4$$

This reaction is the reverse of the dehydration of an ammonium salt, which leads to an amide.

G. Acid Nitriles

The nitriles of carboxylic acids are prepared by alkylation of the salts of hydrocyanic acid:

$$RCl + NaCN \rightarrow R-C \equiv N + NaCl$$

Another route to nitriles is the dehydration of amides carried out by means of phosphoric anhydride or catalytically. Thus, nitriles can be made from ammonium salts of acids by a two-stage dehydration:

$$R-\overset{\overset{O}{\|}}{C}-O^- \overset{+}{N}H_4 \xrightarrow[-H_2O]{\text{pyrolysis}} R-\overset{\overset{O}{\|}}{C}-NH_2$$

$$2R-\overset{\overset{O}{\|}}{C}-NH_2 + P_2O_5 \rightarrow 2R-C \equiv N + 2HPO_3 + H_2O$$

The dehydration can also be accomplished by means of other dehydrating agents, say, phosphorus pentachloride, and in some cases, even acetic anhydride. These reactions are generally carried out at elevated temperatures, which reduces the yield and is convenient not for all amides. A method was proposed in 1970 for preparing nitriles, which makes use of the action of titanium tetrachloride on acid amides in tetrahydrofuran. Good yields are obtained even at 0°C.

The nitrile of formic acid is hydrocyanic acid (hydrogen cyanide). By dehydrating formamide, one can in fact obtain hydrocyanic acid. But at present the most important industrial method of preparing hydrocyanic acid is the Andrussow process, which is the pyrolysis of a mixture of methane and ammonia with an insufficient amount of oxygen:

$$CH_4 + NH_3 + {}^3/_2O_2 \rightarrow HCN + 3H_2O$$

The physical properties of certain carboxylic acid nitriles are given in Table 2.19.

The nitriles possess very little basic character. The conjugate acid of acetonitrile ($CH_3-C\equiv\overset{+}{N}-H$) has a pK_a value of 10 in aqueous solution and a value of 4.2 in anhydrous solvents. Thus, the nitriles are much weaker bases than amides.

The most important reaction of the nitriles is the hydrolysis accomplished by the action of water on heating in acid or alkaline medium. The reaction rate is lower than in the case of all other functional derivatives of carboxylic acids. The reaction occurs in two

TABLE 2.19. The Nitriles of Carboxylic Acids

Formula	Name	m.p., °C	b.p., °C	Density d_4^{20}	Refractive index n_D
HCN	Formonitrile or hydrocyanic acid	—14.0	26.0	0.687	1.2675 (at 10°C)
CH_3-CN	Acetonitrile	—44.0	82.0	0.783	1.3459 (at 16.5°C)
C_2H_5-CN	Propionitrile	—91.9	97.1	0.783 d_4^{21}	1.3688 (at 14.6°C)
n-C_3H_7-CN	Butyronitrile	—112.6	118.0	0.796 (at 15°C)	1.3816 (at 24°C)
$(CH_3)_2CH-CN$	Isobutyronitrile	—71.5	108.0	0.773	1.3720
n-C_4H_9-CN	Valeronitrile	—96.0	141.0	0.801	1.3909 (at 20°C)
$C_{15}H_{31}-CN$	Palmitonitrile	31.0	333	0.830	1.4450
$C_{16}H_{33}-CN$	Margaronitrile	35.5	349	0.831	1.4467
$C_{17}H_{35}-CN$	Stearonitrile	43.0	362	0.832	1.4481
$(CH_3)_2C(CH_3)-CN$	Trimethylacetonitrile	16.0	106.0	—	—

stages and is the inversion of the two stages of dehydration of the ammonium salts of acids given above:

$$R-C\equiv N+H_2O \xrightarrow{H^+} R-\underset{\underset{O}{\|}}{C}-NH_2$$

$$R-\underset{\underset{O}{\|}}{C}-NH_2+H_2O \xrightarrow{H^+} R-\underset{\underset{O}{\|}}{C}-O^- \overset{+}{N}H_4$$

The nitriles also add HCl (analogously to the addition of water at the first stage of hydration):

$$R-C\equiv N+HCl \rightarrow R-\underset{\underset{Cl}{|}}{C}=NH$$

to form **imido-chlorides** of acids—the analogues of acid chlorides. The action of alcohols on imido-chlorides

$$R-\underset{\underset{Cl}{|}}{C}=NH+R'OH \rightarrow R-\underset{\underset{OR'}{|}}{C}=NH$$

gives **imino-ethers** which are the analogues of esters. They can be made by passing HCl into a solution of a nitrile dissolved in the required alcohol.

When the nitriles are alkylated with the salts of tertiary oxonium compounds (page 162), **alkylnitrile salts** are obtained (Meerwein):

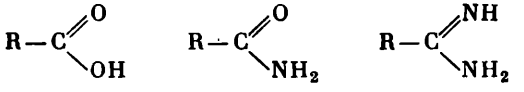
$$R-C\equiv N+(CH_3)_3\overset{+}{O}BF_4^- \rightarrow [R-C\equiv \overset{+}{N}-CH_3]BF_4^- + (CH_3)_2O$$

H. Amidines

When ammonia is reacted with imido-chlorides of the acids, **amidines** are obtained:

$$R-\underset{\underset{Cl}{|}}{C}=NH+2NH_3 \rightarrow R-\underset{\underset{NH_2}{|}}{C}=NH+NH_4Cl$$

The reaction is analogous to the acylation of ammonia with acid chlorides. The amidines themselves are formally analogous to acids (ammonia is an analogue of water):



But, in contrast to carboxylic acids which exhibit relatively weak acidic properties and very slightly basic amides, the amidines are strong bases (for an explanation, see page 235).

Like all the functional derivatives of carboxylic acids, the amidines are hydrolysed to acids.

I. Acid Hydrazides

The acylation of hydrazine leads to the formation of **acid hydrazides**:

$$R-\underset{\underset{O}{\|}}{C}-OR+NH_2-NH_2 \rightarrow R-\underset{\underset{O}{\|}}{C}-NH-NH_2+ROH$$

which give **acid azides** when acted on by nitrous acid:

$$R-\underset{\underset{O}{\|}}{C}-NH-NH_2+HNO_2 \rightarrow R-\underset{\underset{O}{\|}}{C}-N=\overset{+}{N}=\overset{-}{N}$$

Azides are the acylated hydrazoic acid. In fact, the acylation of metal azides also leads to the formation of acid azides:

$$R-\underset{\underset{O}{\|}}{C}-Cl+NaN_3 \rightarrow R-\underset{\underset{O}{\|}}{C}-N=\overset{+}{N}=\overset{-}{N}$$

and the hydrolysis of azides yields a carboxylic acid and hydronitric (hydrazoic) acid:

$$R-\underset{\underset{O}{\|}}{C}-N=\overset{+}{N}=\overset{-}{N}+H_2O \rightarrow R-\underset{\underset{O}{\|}}{C}-OH+HN_3$$

It is in this way that hydrazoic acid was first obtained.

The addition of the sodium derivative of hydrazine to acid nitriles with subsequent hydrolysis of the adduct leads to acid amidrazones:

$$R-C\equiv N+NaNH-NH_2 \rightarrow R-C\begin{matrix}=NNa\\ -NHNH_2\end{matrix} \xrightarrow{H_2O} R-C\begin{matrix}=NH\\ -NHNH_2\end{matrix} \rightleftarrows$$

$$\rightleftarrows R-C\begin{matrix}-NH_2\\ =N-NH_2\end{matrix}$$

J. Hydroxamic Acids

The acylation of hydroxylamine results in the formation of **hydroxamic acids**:

$$R-\underset{\underset{O}{\|}}{C}-Cl+NH_2OH \rightarrow R-\underset{\underset{O}{\|}}{C}-NHOH+HCl$$

These derivatives of hydroxylamine can react as weak acids in two isomeric (tautomeric) forms:

$$R-\underset{\underset{O}{\|}}{C}-NHOH \rightleftarrows R-\underset{\underset{OH}{|}}{C}=NOH$$

All the oxygen and nitrogen functional derivatives of carboxylic acids are related to one another by conversions such that their hydrolysis leads to oxygen-containing derivatives and, in the long run, to a carboxylic acid, and their ammonolysis leads to nitrogen-containing derivatives and eventually to an amidine as the final product.

According to the ease with which the hydrolysis reaction proceeds the simplest derivatives are arranged in the following series:

$$R-\underset{\underset{O}{\|}}{C}-Cl > R-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}-R > R-\underset{\underset{O}{\|}}{C}-OR > R-\underset{\underset{O}{\|}}{C}-NH_2 > R-C\equiv N$$

IV. Factors Responsible for Acidity of Carboxylic Acids. Mesomerism*

The electrolytic dissociation of the sodium salt of a carboxylic acid is often represented schematically as follows:

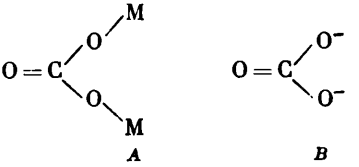
$$R-\underset{\underset{O}{\|}}{C}-ONa \rightleftarrows R-\underset{\underset{O}{|}}{C}-O^- + Na^+$$

But in actual fact the two oxygens in the anion are linked to the carbon absolutely identically and they both, and not one of them, share equally the charge on the anion. In a similar way, as shown by X-ray studies, all the three oxygen atoms in the anion of carbonic acid in a solution of sodium carbonate or in a calcite crystal built of Ca^{2+} and CO_3^{2-} ions are at absolutely equal distances from the carbon atom, and the directions from the centre of the carbon atom to the centres of the oxygens lie in a single plane at the same angle (120°), i.e., the anion has a third-order axis of symmetry. This would be impossible if all the oxygen atoms did not carry equal charges and were not attached to the carbon in an identical manner.

---

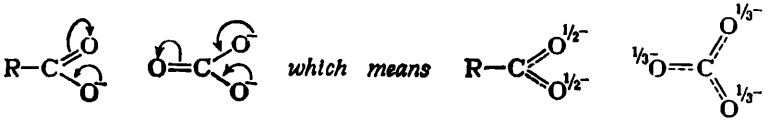
*A stricter treatment of the resonance or mesomerism concept will be given on page 318.

Incidentally, since the undissociated carbonate has the structure *A*, the CO_3^{2-} ion is often depicted by the unsymmetrical formula *B*:



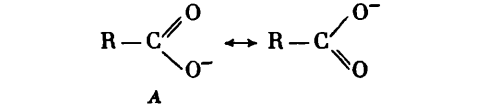
A *B*

In fact, the dissociation is followed by the equalization of the charges and bonds both in the anion of the carboxylic acid and in the carbonate anion, which may be expressed (assuming the notation of the English school of Robinson and Ingold) in the following way:

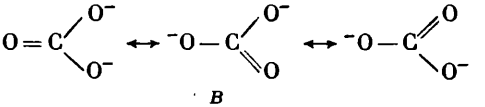


The curved arrows show the shift of free electron pairs on the oxygen atom bearing the charge and the electron pairs of the double bond in the direction of the arrow until the charges are completely equalized and the bonds between the C and O atoms become identical.

Another way of expressing the same phenomenon is to write all the extreme ("canonical") structures and to join them with a single double-headed arrow (↔), which signifies that the actual structure is a hybrid that is intermediate between the structures written (the notation adopted by the American school of Pauling):



A



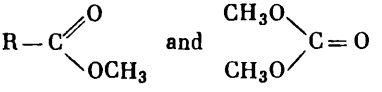
B

Apart from the equilibrium distribution of charges, both notations also express the transition state of the C to O bond which is neither a double bond nor a single bond but is intermediate between these types and can be represented by a fraction: $1^1/_2$ in the *A* system and $1^1/_3$ in the *B* system.

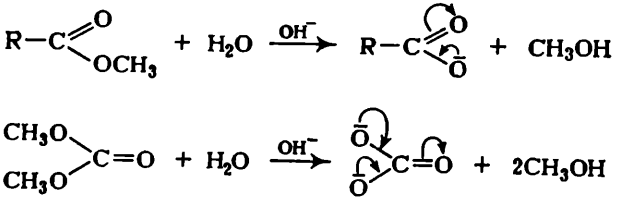
In such cases one speaks of **mesomerism** (the English and German schools) or **resonance** (the American school). This equalization of the bonds and the delocalization of electrons is accompanied by a

lowering of the energy of a molecule as compared with the energy of the hypothetical molecule represented by the extreme (contributing) structures (in the language of the American school) or by a formula (in the symbolism adopted by the English school) without curved arrows. Indeed, since the bond energy of a molecule is an additive quantity made up of the bond energy values of all the bonds in the molecule, it can be calculated for a hypothetical molecule and determined thermochemically for a real molecule (for example, from the heat of combustion). The difference between the actual energy and that calculated for the contributing forms is termed the **resonance energy.** It characterizes the increased stability of such an actual (or "resonating") molecule as compared with hypothetical (nonresonating) molecules.

Hence, in principle, mesomerism or resonance may be looked upon as a phenomenon only with certain reservations. In those cases where such an equilibration (mesomerism or resonance) is possible, it has inevitably taken place, and the hypothetical form is but an abstraction. By the way, since the derivatives of this form exist in a state of mesomerism or resonance, say, in the case of the carboxylate and carbonate anions in esters we are dealing with here:



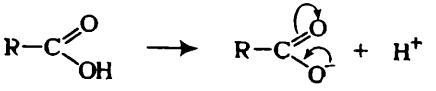
one may speak of the redistribution of electrons and of the equilibration of bonds at the moment of hydrolysis of an ester with alkali, with the formation of an anion. The hydrolysis in fact involves the redistribution of electrons and the transformation of bonds—the process of their equilibration:



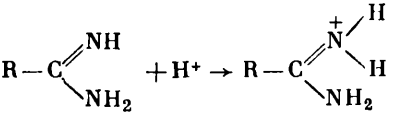
If one diverts from processes of this kind, then mesomerism or resonance provides a means of representing resonating or mesomeric structures through unperturbed or contributing forms which nevertheless have numerous actually existing derivatives.

A lowering of energy upon a change to resonating structures (which is known as the resonance energy) is what serves as the driving force for many processes leading to the formation of mesomeric molecules. This is also responsible for the acidic properties of carboxylic acids.

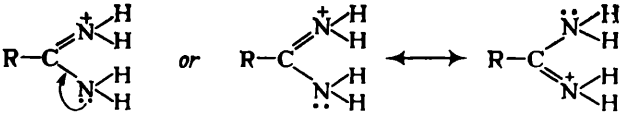
When the molecule of an acid is converted into a pair of ions, the equilibration of electron density (electron delocalization) in the anion is accompanied by a lowering of the energy, i.e., by "a gain of the resonance energy" (of course, meaning that it is decreased by the energy of the heterolytic rupture of the O—H bond and gains the energy of solvation of the cation and anion provided that the process takes place in the solvent). This induces the expulsion of a proton, i.e., the manifestation of acidic properties:



The most complete manifestation of mesomerism or resonance involving a maximum gain in energy occurs upon the attainment of the most symmetrical structures. This is what seems to be responsible for the increased acidic properties of amidines as compared with amides. An amidine that has captured a proton (a hydrogen ion)

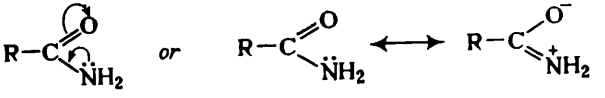


is resonance-stabilized:



Therefore the capture of a proton by an amidine is energetically favourable.

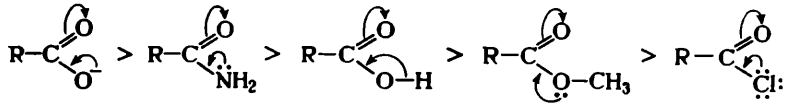
The mesomeric or resonance effect manifests itself also in less symmetrically built molecules. For example, the fact that the amino group in acid amides loses its basic properties may be accounted for by resonance:



Here the mesomeric effect of the NH_2 group is determined as the $+M$ effect and that of the carbonyl group as the $-M$ effect.

The free pair of electrons making possible the capture of a proton and the formation of an ammonium salt (which is the manifestation

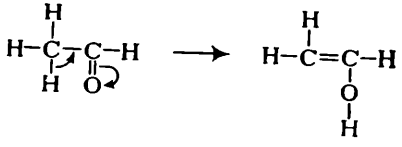
of the basic properties of ammonia and its organic derivatives) in an amide is partly engaged in the formation of a second bond inside the molecule. It is for this reason that nitrogen can hardly add a foreign proton and the basic properties of the amide are suppressed. The same thought may be formulated in a different way: the addition of a proton to nitrogen disturbs the resonance effect, which means that it must have been associated with a loss of resonance energy and not with its gain.



In all carboxylic acids and their derivatives, depending on the degree of resonance of their structures, the positive charge on the carbonyl carbon atom is more or less completely suppressed, and as a result the tendency towards addition or substitution reactions at the carbonyl carbon, which is inherent in aldehydes and ketones, is reduced to a minimum. These two circumstances make the carboxyl group, which is a combination of a carbonyl and a hydroxyl group, a completely new functional group.

The mesomeric effect may be termed the **static effect of conjugation** because it is also inherent in the molecule at rest*, outside the reaction medium. The shift of electron pairs during a reaction, represented by the same curved arrows (the English symbolism), may however go farther, until the pair of electrons is transferred from the octet of one atom to that of another. This effect may be called the **dynamic effect of conjugation.** It is usually termed the **electromeric effect** or more often the **tautomeric effect** (the T effect) since the electron transfer involved in tautomerism is a special case of its manifestation. This effect is designated as $-T$ if the electron pair is removed from the octet of the atom of interest or as the $+T$ effect if the electron pair is transferred to the atom of interest.

The enolization of acetaldehyde is an example of the $-T$ effect of the carbonyl group:



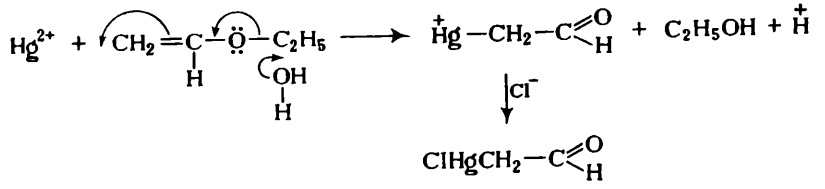
* In other words, the molecule is in the ground, unexcited state. For a more detailed treatment of conjugation, see page 367.

Here the electron pair of the double bond of the carbonyl group has migrated to the oxygen to form a bond with the hydrogen which now belongs to the hydroxyl group formed, and the electron pair which originally linked the hydrogen in the methyl group has moved as a pair of electrons (π-pair) to form a double C=C bond.

Examples of the $-T$ effect have already been encountered in considering ketones and particularly β-diketones; other examples will be found in a section devoted to nitro compounds.

The $-T$ effect, though weaker than in aldehydes and ketones, is also inherent to the carboxyl group of acids.

As an example of the $+T$ effect we may cite the hydrolysis of unsaturated vinyl ethers which readily add a mercury salt, forming a mercuriacetaldehyde ion and an alcohol:



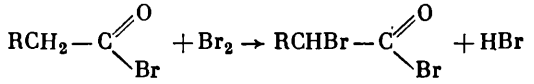
The process depends on the conjugation of the electron orbital of the oxygen and the double C=C bond and also on the ease of transfer of electron pairs by way of the $+T$ effect as a result of the attack on the methylene group by a mercuric ion.

The tautomeric effect exhibits itself in a spectacular way in reactions of unsaturated compounds (see page 420) and in the aromatic series.

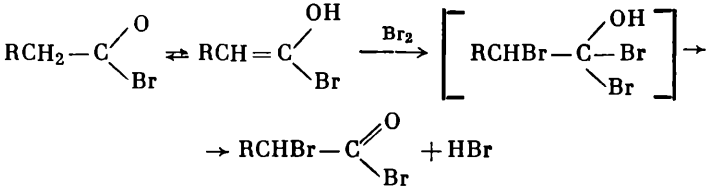
K. Halogen-Substituted Acids

Direct chlorination and bromination of carboxylic acids occurs on heating under the influence of light or in the presence of peroxide catalysts and, like the halogenation of paraffins, is a free-radical process. Using this method, Dumas first prepared mono-, di- and trichloroacetic acids. The halogenation of acids with a longer hydrocarbon chain, however, takes place at different positions. For instance, butyric acid is halogenated chiefly at the β-position, and valeric acid at the β- and γ-positions. For a halogen to be specifically introduced into the α-position, the Hell-Volhard-Zelinsky method is employed, which consists in the halogenation not of the acids themselves but of acid halides. In practice, use is made of acid halides or the bromination of an acid is carried out in the presence of red phosphorus, in which case the phosphorus pentabromide

formed converts the acid into the acid bromide, this being followed by its bromination:

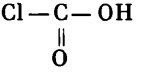


Probably, acid halides are halogenated, like ketones and aldehydes, via the enol which is formed more readily than in acids because of the electron-attracting action of halogen atoms (the $-I$ effect). The enol is formed (the slow stage) in a small amount but it adds halogen rapidly:

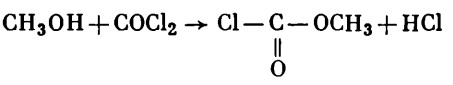


It is for this reason that the substitution occurs at the alpha-carbon atom.

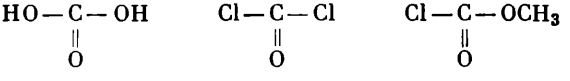
Chloroformic acid



does not exist by itself but its derivatives are known, say, esters. They are prepared by the action of phosgene on alcohols:

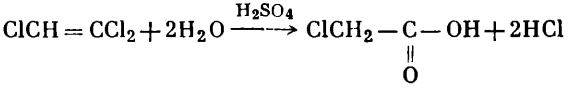


Since phosgene is the chloride of carbonic acid (carbonyl chloride), it may be said, judging by the reaction, that the ester formed is a derivative of carbonic rather than formic acid. It is this derivative that is usually called methyl chlorocarbonate, which is regarded as half-ester of carbonic acid:



The derivatives of chloroformic acid will also be referred to later (Vol. II) as the derivatives of chlorocarbonic acid.

The most common industrial method of preparing **monochloroacetic acid** consists in the hydrolysis of trichloroethylene (see page 354):



The oxidation of ethylene chlorohydrin is also used for the purpose:

$$ClCH_2-CH_2OH \xrightarrow{HNO_3} ClCH_2-\underset{\underset{O}{\|}}{C}-OH$$

Trichloroacetic acid is made by converting alcohol into chloral hydrate by the action of chlorine:

$$CH_3-CH_2OH+4Cl_2+H_2O \rightarrow CCl_3-\underset{\underset{H}{|}}{\overset{\overset{OH}{/}}{C}}\!\!\begin{matrix}\diagup\\\diagdown\end{matrix}\!\!\begin{matrix}OH\\OH\end{matrix}+5HCl$$

followed by the oxidation of chloral hydrate with nitric acid to trichloroacetic acid:

$$CCl_3-\underset{\underset{H}{|}}{\overset{\overset{OH}{/}}{C}}\!\!\begin{matrix}\diagup\\\diagdown\end{matrix}\!\!\begin{matrix}OH\\OH\end{matrix} \xrightarrow{HNO_3} CCl_3-\underset{\underset{O}{\|}}{C}-OH$$

This acid is not inferior to many mineral acids in strength. β-Halogen acids are made by addition of a hydrogen halide to α, β-unsaturated acids, say, to acrylic acid (see page 409):

$$CH_2=CH-\underset{\underset{O}{\|}}{C}-OH+HCl \rightarrow ClCH_2-CH_2-\underset{\underset{O}{\|}}{C}-OH$$

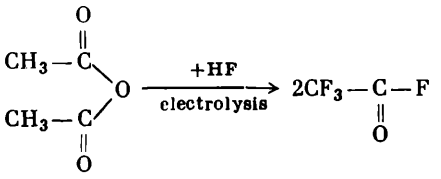
Halogen-substituted acids with a halogen in the ω-position can be obtained from the products of telomerization addition of carbon tetrachloride to olefins (R. Kh. Freidlina; see Volume IV under "Free Radicals"):

$$nCH_2=CH_2+CCl_4 \rightarrow Cl-(CH_2CH_2)_n-CCl_3$$

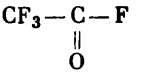
$$Cl-(CH_2CH_2)_n-CCl_3+2H_2O \xrightarrow{H_2SO_4} Cl-(CH_2CH_2)_n-\underset{\underset{O}{\|}}{C}-OH+3HCl$$

An ever increasing importance in preparative organic chemistry is attached to **trifluoroacetic acid** as a very powerful carboxylic acid. It can be made by oxidation of organic compounds containing a $-CF_3$ group, say, by oxidation of perfluoropropylene, $CF_3-CF=CF_2$. But the common method of preparing trifluoroacetic acid is the

electrolysis of a solution of acetic anhydride in anhydrous hydrogen fluoride (the method of electrochemical fluorination):



with the subsequent hydrolysis of the resulting acid fluoride,



V. DISSOCIATION CONSTANTS OF HALOGEN-SUBSTITUTED ACIDS. THE INDUCTIVE EFFECT

As the hydrogen atoms contained in the chain of a carboxylic acid are substituted by halogen atoms the dissociation constant of the acid increases. This effect is particularly pronounced when the hydrogen atoms are replaced in the alpha-position (see Table 2.20).

TABLE 2.20. **The Dissociation Constants of Halogen-Substituted Acetic Acids in Water at 25°C**

Fluoro acids	K_a	Chloro acids	K_a	Bromo acids	K_a
FCH_2COOH	21×10^{-3}	$ClCH_2COOH$	1.40×10^{-3}	$BrCH_2COOH$	2.05×10^{-3}
$F_2CHCOOH$	57×10^{-2}	$Cl_2CHCOOH$	3.32×10^{-2}	—	—
F_3CCOOH	5.9×10^{-1}	Cl_3CCOOH	2.0×10^{-1}	—	—

The influence of halogen is accounted for by the fact that the alpha-carbon attached to halogen, especially to fluorine, becomes more positively charged than in the case of its attachment to hydrogen. In other words, the electron pairs of the bond are attracted toward the halogen atoms, leaving the carbon with a positive charge. The more positive alpha-carbon atom in its turn attracts a pair of electrons binding it to the carboxyl carbon atom. This carbon becomes more positive than the ordinary carboxyl carbon and withdraws more electron pairs that bind it to the oxygen. As a result, the carboxyl hydrogen (proton) is found to be less firmly bound to the oxygen.

A similar picture is observed not only on α-substitution but also in the case of a more remote halogen atom:

	K_a (at 25°C)
Butyric acid, $CH_3CH_2CH_2COOH$	1.54×10^{-5}
α-Chlorobutyric acid, $CH_3CH_2\underset{\displaystyle Cl}{\underset{|}{C}}HCOOH$	1.39×10^{-3}
β-Chlorobutyric acid, $CH_3\underset{\displaystyle Cl}{\underset{|}{C}}HCH_2COOH$	8.9×10^{-5}
γ-Chlorobutyric acid, $\underset{\displaystyle Cl}{\underset{|}{C}}H_2CH_2CH_2COOH$	3.0×10^{-5}

The effect of halogen diminishes rapidly as the halogen is moved, along a chain of carbon atoms, farther from the carboxyl and is hardly noticeable on γ-substitution. This effect drops off less markedly only in the case of a very strong electron-attracting group.

The dissociation constants, K_a, of a number of saturated ω,ω,ω-trichlorosubstituted acids in 50-percent (by weight) methanol have the following values (R. Kh. Freidlina and L. I. Zakharkin):

$CCl_3(CH_2)_4COOH$	4.6×10^{-6}
$CCl_3(CH_2)_6COOH$	1.5×10^{-6}
$CCl_3(CH_2)_8COOH$	1.25×10^{-6}
$CCl_3(CH_2)_{10}COOH$	9.55×10^{-7}
$CCl_3(CH_2)_{12}COOH$	8.95×10^{-7}

Substitution by a halogen will naturally not only enhance the acidic properties of compounds but simultaneously weaken their basic properties, and the effect will also diminish with chain lengthening. This is seen from the data obtained by the same authors for a series of ω,ω,ω-trichloroalkylamines (in water at 20°C):

	K_b
$CCl_3CH_2NH_2$	2×10^{-9}
$CCl_3(CH_2)_2NH_2$	3×10^{-5}
$CCl_3(CH_2)_3NH_2$	6×10^{-5}
$CCl_3(CH_2)_4NH_2$	9×10^{-5}

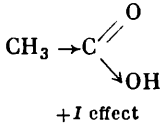
This phenomenon is of general importance in organic chemistry and is known as the **inductive effect** (the *I* effect). It may operate in two opposite directions.

The effect of the chlorine atom considered above is an example of the *negative inductive effect* (symbolized as $-I$). It enhances the acidic properties of the key group of atoms and weakens its basic properties. The opposite effect (the *positive inductive* or $+I$ *effect*) is characteristic of the replacement of hydrogen by methyl and,

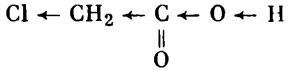
in general, alkyl groups. It may be exemplified by the familiar case of lowering of acidity in the homologous series of formic acid:

	K_a (at 25°C)	pK
HCOOH	1.72×10^{-4}	—
CH_3COOH	1.76×10^{-5}	4.75
CH_3CH_2COOH	1.34×10^{-5}	4.87
$CH_3(CH_2)_2COOH$	1.54×10^{-5} (at 20°C)	4.81
	K_a (at 18°C)	pK
$CH_3(CH_2)_3COOH$	1.51×10^{-5}	4.82
$CH_3(CH_2)_4COOH$	1.43×10^{-5}	4.83
$(CH_3)_3CCOOH$	9.4×10^{-6}	5.03

The inductive effect is graphically shown by a straight arrow placed between the atoms so as to indicate the direction in which the electrons tend to move:

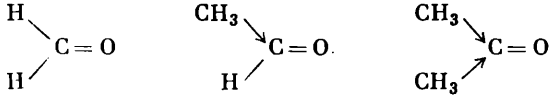


+*I* effect

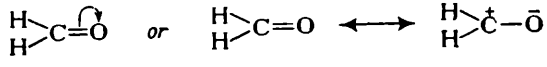


−*I* effect

The inductive effect brings about a change not only in the acidic or basic properties of compounds on substitution but also in the various manifestations of reactivity. We have already met with this effect in the discussion of the various degrees of reactivity of the carbonyl group in aldehydes and ketones:

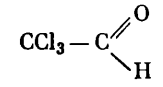


In this series, formaldehyde is the most and acetone the least reactive. This is associated with the fact that the reactivity of the carbonyl group is due to the separation of the charges on carbon and oxygen:



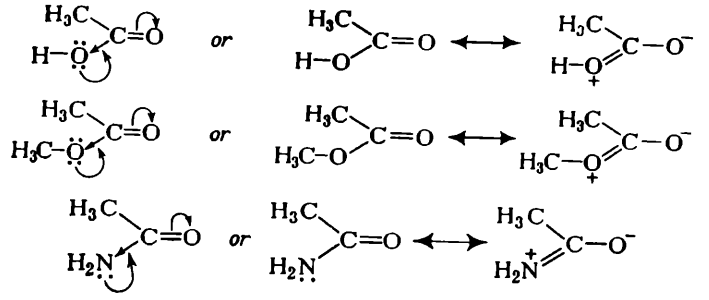
and the reaction centre of the carbonyl group is the positively charged carbon. The replacement of hydrogen by a methyl group and, to an even greater extent, the introduction of two methyl groups suppress the positive charge on the carbonyl carbon because of the bonding electron pairs being drawn to it.

The $-I$ effect is exhibited, as we have seen, by the CCl_3 group as a whole (due to the $-I$ effects of three chlorine atoms). Therefore, the carbonyl group of chloral



reacts more vigorously in addition (and substitution) reactions than the carbonyl group of acetaldehyde and its homologues. This also accounts for the addition of water to chloral with the formation of chloral hydrate.

One may be confused by the fact that the introduction of a hydroxyl or an alkoxyl group (groups exerting an $-I$ effect) in place of the hydrogen of the aldehyde group does not display a noticeable $-I$ effect on the carbonyl carbon but rather has a clearly opposite action, repressing the reactivity of the carbonyl group which is "dead" in acetic acid, its esters and in an amide and resembles neither the aldehyde nor the keto group. The reason is that we are dealing here with a different phenomenon—the familiar mesomeric effect (see page 235) which is expressed in different ways:

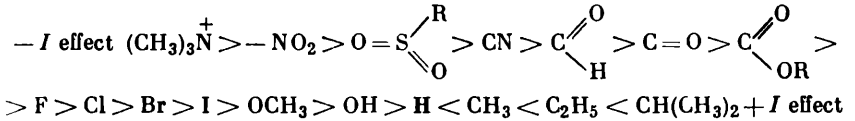


This phenomenon is always more pronounced than the inductive effect and overlaps it.

Thus, the inductive effect is an effect which is transmitted through a chain of saturated atoms and their single bonds and which diminishes rapidly. The mesomeric (or resonance) effect is transmitted along a chain of conjugated double bonds and is repressed but a little.

It should be specially stressed that the concept of the $-I$ or $+I$ effect arises only when the properties of an unsubstituted compound are compared with those of substitution products, i.e., the hydrogen atom is used as an arbitrary standard for comparison. All other atoms and groups are arranged to the left (the $-I$ effect) and to the

right (the $+I$ effect) from the hydrogen atom, approximately in the following order:



L. Dibasic Carboxylic Acids

The names and physical properties of dibasic (or dicarboxylic) acids (acids containing two carboxyl groups) with unbranched chains are listed in Table 2.21. This series of acids is usually regarded as a homologous series since each member differs from the previous one by a methylene group and the functions of all the members are identical. But, as can be easily noticed, each succeeding member of the series cannot be formed from the previous one by means of the familiar (mental) operation—the replacement of the hydrogen atom in the skeleton by a methyl group.

TABLE 2.21. **Saturated Dibasic Acids**

Formula	Name of acid		
	trivial	Geneva	carboxylic system
HOOC—COOH	Oxalic	Ethanedioic	—
HOOC—CH_2—COOH	Malonic	Propanedioic	Methanedicarboxylic
HOOC—$(CH_2)_2$—COOH	Succinic	Butanedioic	1,2-Ethanedicarboxylic
HOOC—$(CH_2)_3$—COOH	Glutaric	Pentanedioic	1,3-Propanedicarboxylic
HOOC—$(CH_2)_4$—COOH	Adipic	Hexanedioic	1,4-Butanedicarboxylic
HOOC—$(CH_2)_5$—COOH	Pimelic	Heptanedioic	1,5-Pentanedicarboxylic
HOOC—$(CH_2)_6$—COOH	Suberic	Octanedioic	1,6-Hexanedicarboxylic
HOOC—$(CH_2)_7$—COOH	Azelaic	Nonanedioic	1,7-Heptanedicarboxylic
HOOC—$(CH_2)_8$—COOH	Sebacic	Decanedioic	1,8-Octanedicarboxylic

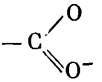
Except the first member of the series, all the succeeding dibasic acids have an infinite series of homologues in the ordinary, narrower sense of this word, which are not listed in the table and which are formed by replacement of the hydrogen in the methylene groups of the skeleton by a methyl or a homologous group.

The first two right-hand columns of the table indicate the values of K_{a1} and K_{a2}, i.e., the dissociation constants of the first and second carboxyls in dilute aqueous solutions. A comparison of these two constants shows the powerful mutual inductive effect of two carboxyl groups, which increases the first dissociation constant (as compared

TABLE 2.22. **Properties of Saturated Dibasic Acids**

Formula	m.p., °C	b.p., °C	Solubility in water at 20°C, g/100 g	Dissociation constants in water at 25°C	
				K_{a1}	K_{a2}
HOOC—COOH	189.0 (anhydr.)	150 (subl.)	9.5 (at 15°C)	5.90×10^{-2}	6.4×10^{-5}
HOOC—CH_2—COOH	135.6	Dec.	73.5	1.49×10^{-3}	2.03×10^{-6}
HOOC—$(CH_2)_2$—COOH	185.0	235 (dec.)	6.8	6.89×10^{-5}	2.47×10^{-6}
HOOC—$(CH_2)_3$—COOH	97.5	304 (dec.)	64.0	4.55×10^{-5}	3.89×10^{-6}
HOOC—$(CH_2)_4$—COOH	153	265 (at 100 mm Hg)	1.5 (at 15°C)	3.71×10^{-5}	3.87×10^{-6}
HOOC—$(CH_2)_5$—COOH	103.0	272 (subl. at 100 mm Hg)	5.0	3.09×10^{-5}	3.77×10^{-6}
HOOC—$(CH_2)_6$—COOH	140.0	279 (at 100 mm Hg)	0.14 (at 16°C)	2.99×10^{-5}	2.5×10^{-6} (at 100°C)
HOOC—$(CH_2)_7$—COOH	106.5	226 (at 10 mm Hg)	0.24	2.88×10^{-5}	2.8×10^{-6}
HOOC—$(CH_2)_8$—COOH	133.0	295 (at 100 mm Hg)	0.10 (at 17°C)	2.60×10^{-5}	2.6×10^{-6} (at 100°C)

with monobasic acids). After the first hydrogen ion has dissociated and the charged anion group



has formed, the situation sharply changes and the second dissociation constants become lower than in the case of monocarboxylic acids.

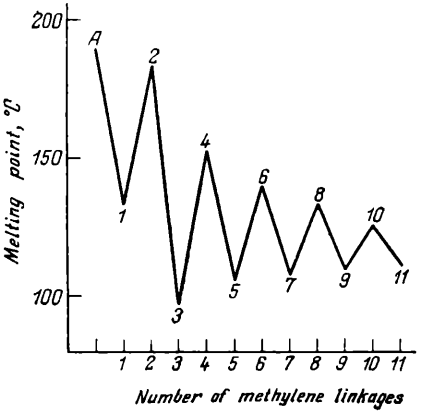


Fig. 2.4.

The melting points of dibasic saturated normal acids:

A—oxalic acid; *1*—malonic acid; *2*—succinic acid; *3*—glutaric acid; *4*—adipic acid; *5*—pimelic acid; *6*—suberic acid; *7*—azelaic acid; *8*—sebacic acid; *9*—1,9-nonanedicarboxylic acid; *10*—1,10-decanedicarboxylic acid; *11*-brassylic acid.

This is natural since the negative charge of the carboxylate anion does not allow the hydrogen of the second carboxyl group to dissociate.

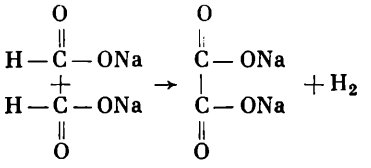
The melting points of straight-chain dibasic acids in the homologous series change alternatively, as seen from Fig. 2.4. Acids with an even number of carbon atoms melt at a higher temperature than those with an odd number of carbon atoms (the difference decreases with lengthening of the carbon chain). With the direction of valency bonds, which are at 109° relative to each other at a saturated carbon atom, being taken into account, the regular rise and fall of melting point is usually explained as due to the alternation in the position of the carboxyl groups of even and uneven members of the homologous series.

Here one should take into account the various (geometrical) conditions of the formation of hydrogen bonds in the two carboxyl groups of even and odd members of the series (page 209).

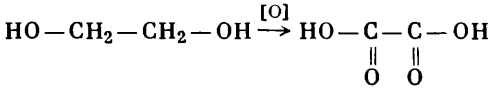
The solubility of acids in water also changes in a zigzag manner with increasing molecular weight.

(a) *Preparation of Dicarboxylic Acids*

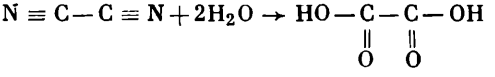
Oxalic acid, which occupies a special place in the series as the first member, is formed during the oxidation of many organic compounds. For example, when sugar is oxidized by nitric acid, the products obtained also include oxalic acid. Until relatively recently oxalic acid has beed made on an industrial scale from wood by oxidative fusion with alkali. At present, it is produced industrially by heating sodium formate:



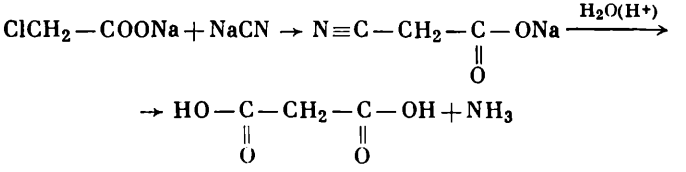
Evidently, the oxidation of ethylene glycol as a primary alcohol will also lead to oxalic acid:



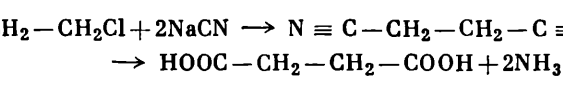
It is interesting to note that the first synthetic route to oxalic acid was the hydrolysis of its nitrile—cyanogen (Wöhler, 1824):



Malonic acid is always prepared via its mononitrile—cyanoacetic acid:

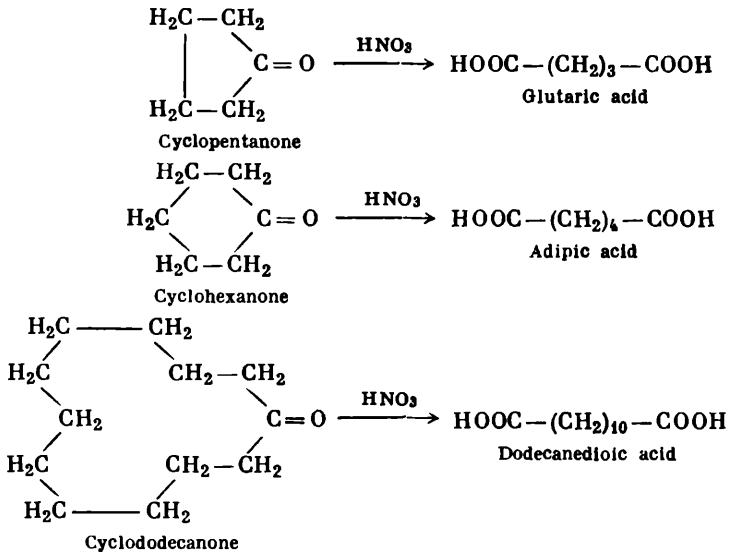


Succinic acid can be synthesized via its dinitrile:



Succinic acid can also be obtained by the hydrogenation of maleic acid (page 422) or by the Conrad synthesis via sodiomalonic ester (page 254).

The most general method of synthesizing higher dibasic acids (dicarboxylic acids) is the oxidation of cyclic ketones:



Higher dicarboxylic acids can also be made from tetrachloroalkanes, $Cl-(CH_2)_2-CCl_3$ (A. N. Nesmeyanov, R. Kh. Freidlina, L. I. Zakharkin) by the following two methods:

(a) the even-carbon members of the series:

$$Cl-(CH_2CH_2)_n-CCl_3 \xrightarrow{NaCN} N\equiv C-(CH_2CH_2)_n-CCl_3 \xrightarrow{H_2O(H_2SO_4)} \rightarrow HOOC-(CH_2CH_2)_n-COOH$$

(b) the odd-carbon members:

$$Cl-(CH_2CH_2)_n-CCl_3 \xrightarrow{H_2O(H_2SO_4)} Cl-(CH_2CH_2)_n-COOH \xrightarrow{NaOH} \rightarrow HO-(CH_2CH_2)_n-COONa \xrightarrow{O} HOOC-CH_2-(CH_2CH_2)_{n-1}-COOH$$

The tetrachloroalkanes required for this purpose are synthesized from ethylene and carbon tetrachloride by the telomerization reaction (see Volume III, "Free Radicals").

Acids with an even number of carbon atoms can be made by the Kolbe reaction (page 214) through the electrolysis of salts of acid esters of the lower dibasic acids:

$$2C_2H_5-O-\overset{\overset{O}{\|}}{C}-(CO_2)_n-\overset{\overset{O}{\|}}{C}-O^- \xrightarrow[-2e]{} 2C_2H_5-O-\overset{\overset{O}{\|}}{C}-(CH_2)_n-\overset{\overset{O}{\|}}{C}-O\cdot \rightarrow$$

$$\rightarrow 2CO_2+C_2H_5-O-\overset{\overset{O}{\|}}{C}-(CH_2)_{2n}-\overset{\overset{O}{\|}}{C}-OC_2H_5$$

(b) *Specific Chemical Behaviour of Dicarboxylic Acids*

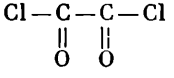
All that has been said about the properties of the carboxylic function (page 205) is naturally also applicable to dicarboxylic acids. Here we shall consider only the specific features of the behaviour of various types of dibasic acids.

The first member of the series, *oxalic acid*, is one of the strongest carboxylic acids, which by far exceeds its homologues in strength. It crystallizes with two water molecules (the melting point of the hydrate is 101.5°C), which can be eliminated by distilling off the water, say, with CCl_4 vapours, anhydrous oxalic acid being obtained as a result.

In contrast to its homologues, oxalic acid is readily oxidized by strong oxidizing agents, say, $KMnO_4$, in acid medium, forming carbon dioxide and water. When oxalic acid is heated with sulphuric acid, it decomposes with the evolution of CO, CO_2 and H_2O.

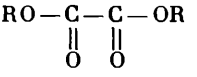
Oxalic acid forms no anhydride. It gives two series of derivatives on replacement of one or both carboxyl groups. For example,

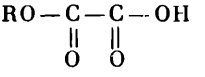
Acid halide



Oxalyl chloride

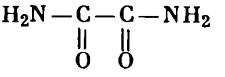
Esters

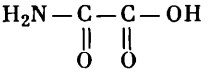




Acid ester

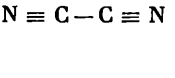
Amides

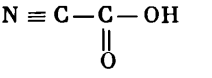




Oxamide | Oxamic acid

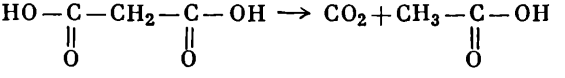
Nitriles





Cyanogen | Cyanoformic acid

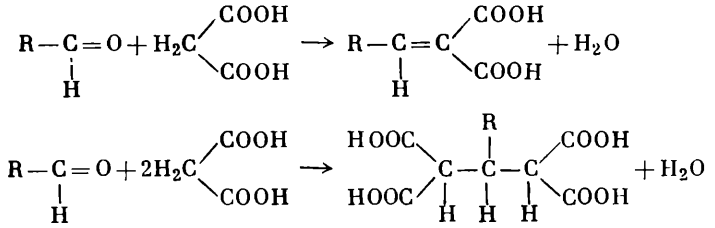
Malonic acid also has specific features which sharply distinguish it from the succeeding members of the series (succinic acid, etc.). When heated (135°C) malonic acid decarboxylates smoothly, forming acetic acid:



This property is retained by all the immediate homologues of malonic acid, i.e., alkylmalonic acids.

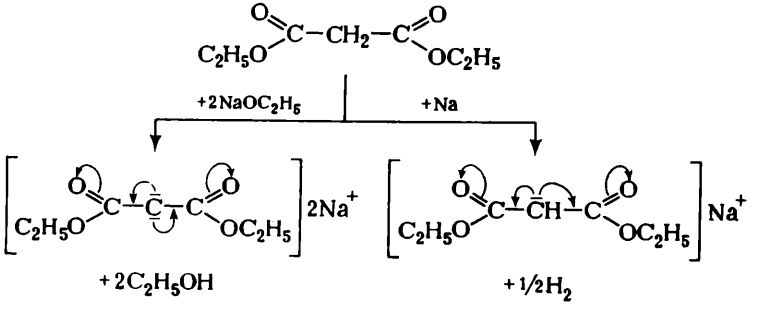
The two hydrogen atoms of the methylene group in malonic acid are in the alpha position relative to the two carboxyls and are therefore much more replaceable than in monobasic (monocarboxylic)

acids. As an example, malonic acid enters especially readily into reactions of condensation with aldehydes (base-catalysed). Depending on the conditions and the ratio of the reagents, one or two molecules of the acid react with an aldehyde molecule:



Malonic acid is easily halogenated into the alpha position.

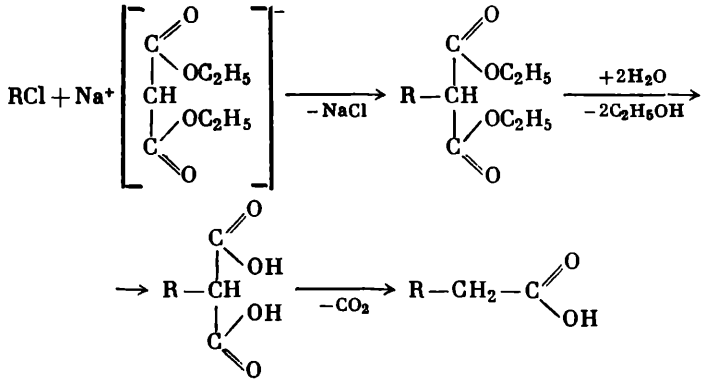
The mobility of the hydrogens of the alpha-methylenic link is especially conveniently observed in the esters of malonic acid, containing no acid hydrogens of the carboxyl groups, which are the most mobile and which could obscure the picture. When the ethyl ester of malonic acid (ethyl malonate or malonic ester) is reacted with metallic sodium or sodium alkoxide, one hydrogen atom of the methylene group or both hydrogens (if an excess of metallic sodium is present) are replaced by sodium and sodiomalonic (or, respectively, disodiomalonic) ester is formed, which has found wide use in synthesis:



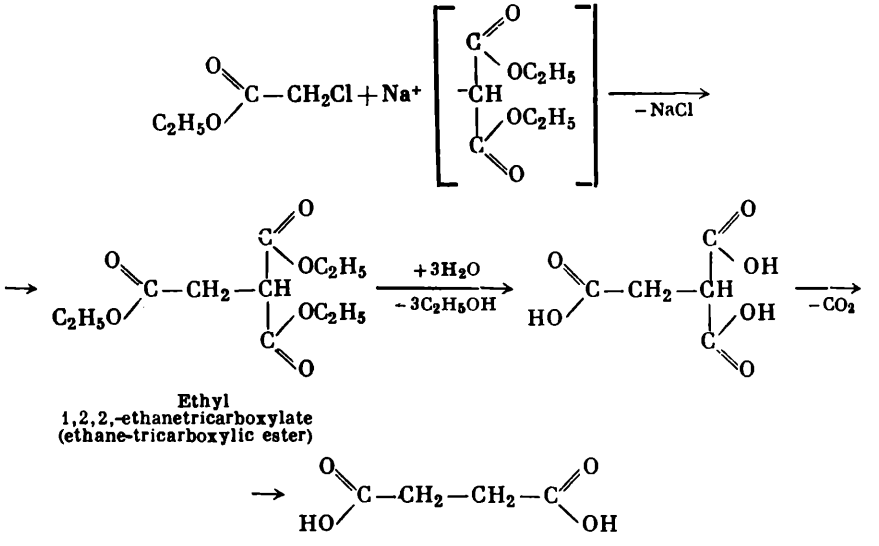
When sodiomalonic ester is acted on by alkyl halides or other halogen derivatives with a sufficiently mobile halogen, the halogen is split off in the form of a sodium salt and the sodium in the methylene group is replaced by an alkyl or other radical formerly attached to the halogen. In this way, the homologues and various other substituted malonic esters can be prepared, whose hydrolysis can give acids (the Conrad synthesis). One of the "malonic" carboxyls can be removed by decarboxylation and the homologues or other substituted derivatives of acetic acid produced. Thus, the Conrad synthesis is an important and versatile method for synthesis of mono-

basic and polybasic acids. Examples of the Conrad synthesis are given below.

1. Synthesis of the homologues of acetic acid:

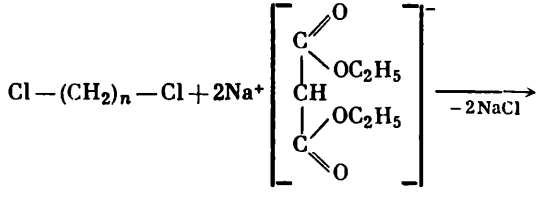


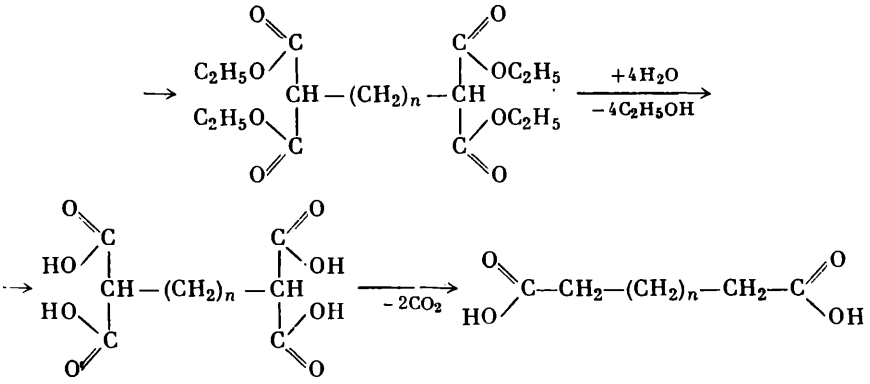
2. Synthesis of succinic acid:



Ethyl
1,2,2,-ethanetricarboxylate
(ethane-tricarboxylic ester)

3. Synthesis of glutaric and other dibasic acids:

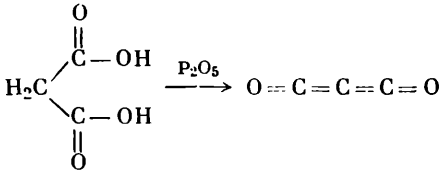




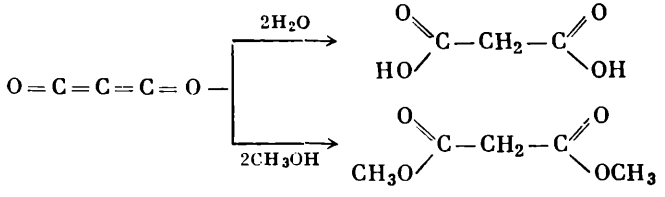
The use of sodiomalonic ester for synthesis of alicyclic carboxylic acids will be described in Volume II.

From the previously given reactions of condensation of malonic acid with aldehydes it follows that this pathway can also be used for synthesizing monobasic unsaturated and dibasic saturated acids.

Of the other properties of malonic acid, mention should be made of its behaviour during the dehydration by phosphorus pentoxide, which yields **carbon suboxide**:



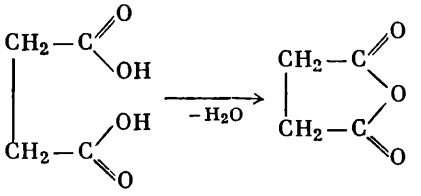
The mobility of alpha-hydrogen atoms also plays a part in this reaction. Carbon suboxide belongs to the category of ketenes and behaves as a sort of malonic acid anhydride:



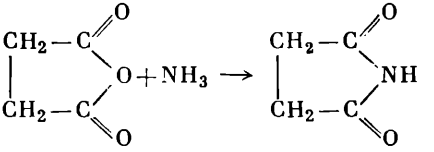
Malonic acid forms no ordinary anhydride.

Succinic acid differs from the preceding members of the series in that it forms cyclic functional derivatives, namely, anhydrides and imides. When heated for a long time or, what is better, when dehydra-

ted by acetic anhydride, succinic acid gives succinic anhydride:



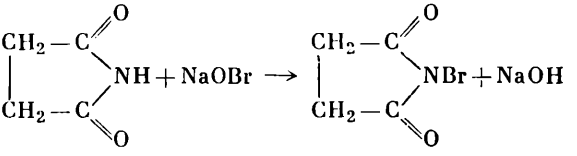
which has the usual properties of acid anhydrides. For example, the interaction with ammonia yields an imide (**succinimide**):



There also exists an amide of succinic acid, which is formed by the action of ammonia on the acid chloride or ester of succinic acid.

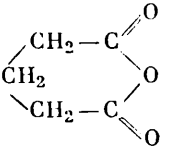
The basic properties of succinimide are even weaker than those of the amides. On the contrary, the hydrogen of its imino group can easily be removed as a proton. For example, under the action of alkali metal alkoxides the hydrogen of the imino group is replaced by the metal and potassium or sodium succinimide is formed as a result.

N-Bromosuccinimide has recently become very important as a brominating agent. It is obtained from succinimide by the action of NaOBr:



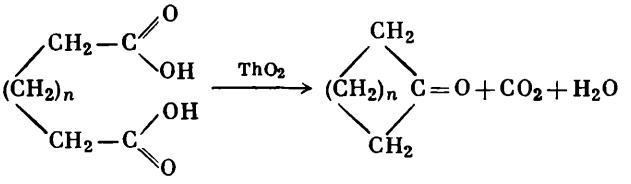
With its aid it is possible to substitute a methylene hydrogen for bromine at the alpha-position relative to the olefinic bond (page 344).

Glutaric acid also forms a cyclic anhydride:



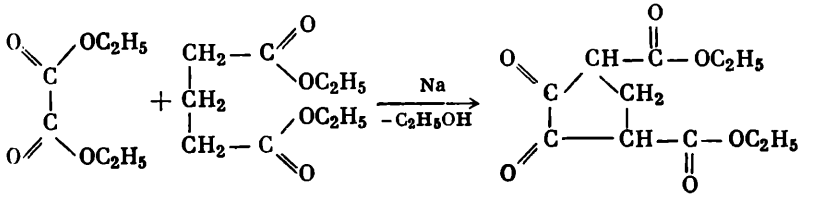
The higher dibasic acids do not form such cyclic functional derivatives. They give two series of functional derivatives which are similar to the corresponding derivatives of monocarboxylic acids.

Dibasic acids can be converted into five- and six-membered alicyclic compounds either directly by a catalytic reaction over thorium (or manganese) oxide:

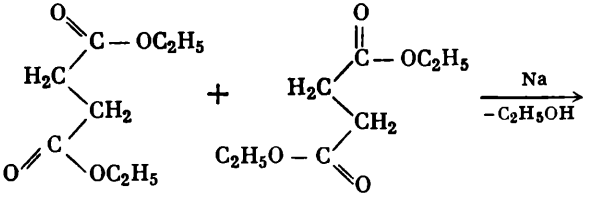


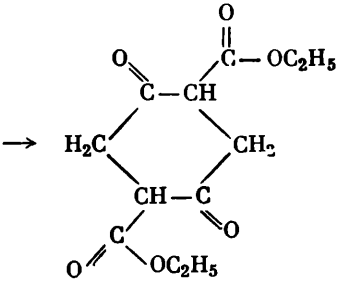
(n=2 or 3)

or, in the form of esters, by the action of sodium as the result of ester condensation (Volume II), which leads to the formation of keto acid esters with five- and six-membered rings (the Dieckmann reaction):

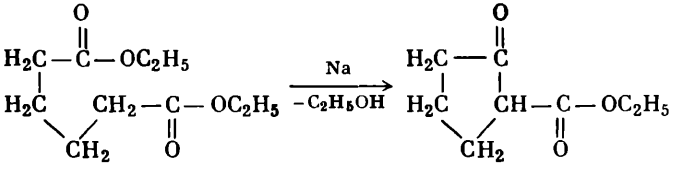


(1)





(2)



(3)

Thus, the dibasic aliphatic acids are valuable starting compounds for synthesis of alicyclic compounds.

(c) *Uses of Dicarboxylic Acids*

Oxalic acid is used in the textile industry as a relatively strong organic acid. Some of the higher dibasic acids, in particular sebacic acid, find application, in the form of their butyl and also octyl esters, as plasticizers in the production of plastics and as high-quality lubricating greases. Adipic acid is used for producing the polymer Nylon, from which fibres are made.

2.11. Organic Derivatives of Hydrogen Peroxide

Hydrogen peroxide is a substance which is electrolytically slightly dissociated ($K_a = 1.55 \times 10^{-12}$), though more dissociated than water. When being alkylated or acylated hydrogen peroxide (or sodium peroxide) forms mono- and dialkyl (or mono- and diacyl) derivatives, the synthesis of which is exemplified by the more stable *tert*-butyl and acetyl derivatives:

$$2(CH_3)_3CCl + Na_2O_2 \longrightarrow \underset{\textit{tert}\text{-Butyl peroxide}}{(CH_3)_3C-O-O-C(CH_3)_3} + 2NaCl$$

$$(CH_3)_3COH + H_2O_2 \xrightarrow{H^+} \underset{\textit{tert}\text{-Butyl hydroperoxide}}{(CH_3)_3C-OOH} + H_2O$$

$$2CH_3-\overset{\overset{O}{\|}}{C}-Cl + Na_2O_2 \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-O-O-\overset{\overset{O}{\|}}{C}-CH_3 + 2NaCl$$

Acetyl peroxide

$$2CH_3-\overset{\overset{O}{\|}}{C}-Cl + H_2O_2 + NaOH \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-OOH + NaCl + H_2O$$

or, what is better, by the following:

$$CH_3-\overset{\overset{O}{\|}}{C}-O-O-\overset{\overset{O}{\|}}{C}-CH_3 + NaOC_2H_5 \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-OONa + CH_3-\overset{\overset{O}{\|}}{C}-OC_2H_5$$

$$\downarrow H^+$$

$$CH_3-\overset{\overset{O}{\|}}{C}-OOH$$

Acetyl hydroperoxide
(peracetic acid)

Acyl hydroperoxides possess weak acidic properties and form salts and esters (peresters) which may also be regarded as mixed alkyl-acyl peroxides:

$$R-OOH+R'-\underset{\underset{O}{\|}}{C}-Cl \xrightarrow[-NaCl]{NaOH} R-O-O-\underset{\underset{O}{\|}}{C}-R' \xleftarrow{-NaCl} R'-\underset{\underset{O}{\|}}{C}-OONa+RCl$$

There also exist mixed alkyl-alkyl and acyl-acyl peroxides, the synthesis of which can be ascertained from the above reaction.

The physical properties of the simplest peroxides are given in Table 2.23.

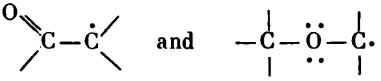
Alkyl hydroperoxides also result from the interaction of free alkyl radicals with a free oxygen which itself is a biradical, ·O—O· (it is in the triplet state, see Volume III, "Free Radicals"):

$$R\cdot + \cdot O-O\cdot \longrightarrow R-O-O\cdot$$

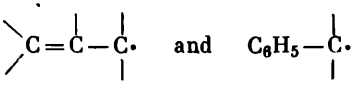
$$R-O-O\cdot + RH \longrightarrow R-O-O-H+R\cdot$$

and so on.

The chain can be propagated, however, only if the radical R· is stabilized (has a decreased energy) due to the distribution of an unpaired electron. This is possible when the carbon atom carrying an unpaired electron is adjacent to an atom having a double bond or to one bearing an unshared pair of electrons. In the classes of compounds already studied, these are the groupings

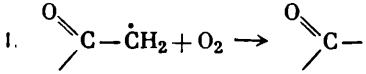


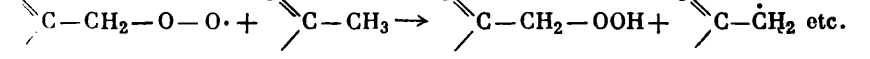
which have been encountered in aldehydes and ketones and also in others. In structures to be studied later these are the groupings



Saturated hydrocarbons undergo oxidation of this kind only at a high "preflame" temperature.

The chain reactions of oxidation of a stabilized radical with free oxygen take place according to the following schemes:

I. 



II. $CH_3CH_2-\ddot{O}-\dot{C}HCH_3+O_2 \longrightarrow CH_3CH_2-\ddot{O}-\underset{\underset{OO\cdot}{|}}{C}HCH_3$

TABLE 2.23. **Hydroperoxides, Peroxides and Peresters**

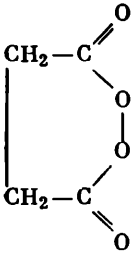
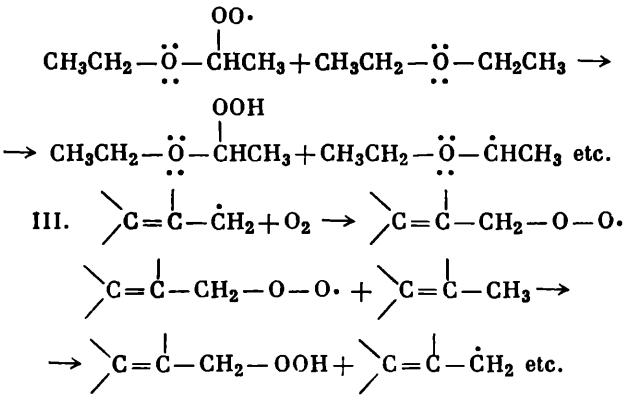
Formula	Name	m.p., °C	b.p., °C	Density d_4^{20}
	Alkyl hydroperoxides			
CH_3-OOH	Methyl hydroperoxide	—	38—40 (at 65 mm Hg)	0.936
C_2H_5-OOH	Ethyl hydroperoxide	—100	97	
$(CH_3)_3C-OOH$	*tert*-Butyl hydroperoxide	6	5 (at 2 mm Hg)	0.896
	Alkyl peroxides			
$CH_3-OO-CH_3$	Methyl peroxide	—	13.5 (at 740 mm Hg)	0.80-0.85
$C_2H_5-OO-C_2H_5$	Ethyl peroxide	—70	65	0.827 d_4^{11}
$(CH_3)_3-OO-C(CH_3)_3$	*tert*-Butyl peroxide	—40	70 (at 197 mm Hg)	0.794
	Acyl hydroperoxides			
$H-\overset{\overset{O}{\|}}{C}-OOH$	Formyl hydroperoxide or performic acid	80 (expl.)	—	—
$CH_3-\overset{\overset{O}{\|}}{C}-OOH$	Acetyl hydroperoxide or peracetic acid	0.1	25 (at 12 mm Hg)	1.226 d_4^{15}
	Acyl peroxides			
$CH_3-\overset{\overset{O}{\|}}{C}-OO-\overset{\overset{O}{\|}}{C}-CH_3$	Acetyl peroxide	26-27	63 (at 21 mm Hg)	—
	Succinyl peroxide	100 (expl.)	—	—

TABLE 2.23. (continuation)

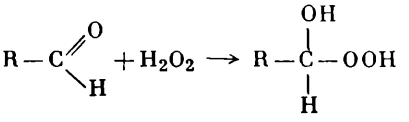
Formula	Name	m.p., °C	b.p., °C	Density d_4^{20}
	Peracid esters (*peresters*)			
$(CH_3)_3COO-C(=O)-C_{18}H_{37}$	*tert*-Butyl perstearate	14-16.5	186 (at 3 mm Hg)	—
$(CH_3)_3COO-C(=O)-CH_2$ $(CH_3)_3COO-C(=O)-CH_2$	Di-*tert*-butyl persuccinate	53-54	—	—
$(CH_3)_3COO-C(=O)-C_6H_5$	*tert*-Butyl perbenzoate	—	75-77 (at 2 mm Hg)	1.043
$(CH_3)_3COO-C(=O)-OC_2H_5$	*tert*-Butyl-ethyl percarbonate	52-55 (at 1 mm Hg)	—	0.966



As a result of such an oxidation in air, which is however very slow, the ethyl ether which has been in contact with the air, and which often contains a hydroperoxide of the indicated structure, presents therefore a hazard on distillation; after the major portion of the ether has been distilled off there remains an explosive hydroperoxide. Prior to distillation the ether must be freed from the peroxide, if there is any, by washing with water (the presence of peroxide is established with the aid of KI or Fe^{2+}).

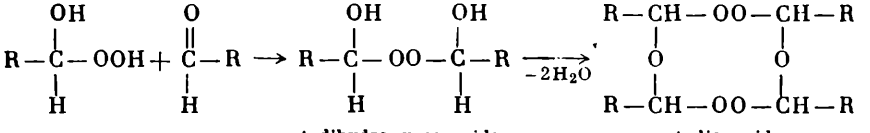
Aldehydes and ketones when reacted with hydrogen peroxide in acid medium give peroxide compounds (Table 2.24), the formation of which involves a carbonyl group and not an alpha-hydrogen atom.

The first stage of the reaction is the addition of hydrogen peroxide to the carbonyl group with the formation of a hydroxyhydroperoxide:



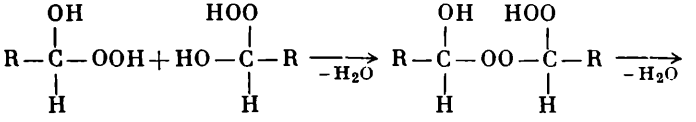
An α-hydroxyhydroperoxide

Then, depending on the conditions and the presence of an excess of any of the starting or intermediate compounds, the reaction may take different routes:

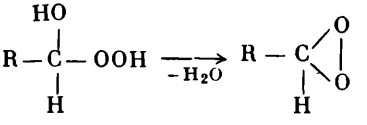


A dihydroxy peroxide

A diozonide



An aldehyde diperoxide



Especially unstable are the inner peroxides of the last-named type.

All the types of structures given also exist for ketones. The properties of the peroxides formed by aldehydes and ketones are presented in Table 2.24.

Alkyl peroxides (particularly, the most stable *tert*-butyl peroxide), acyl peroxides (acetyl and benzoyl peroxides) and also percarbonates of the general formula

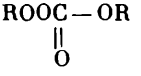
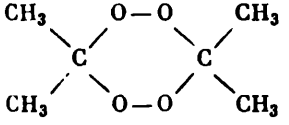
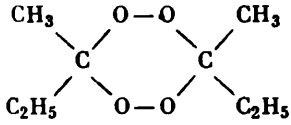
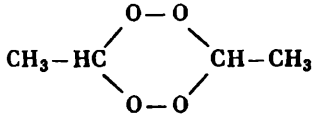
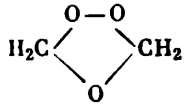
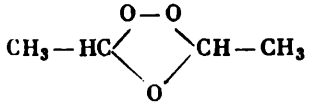
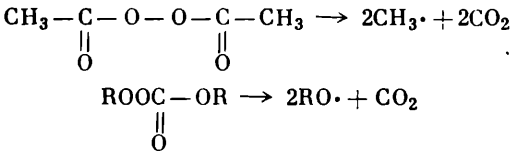


TABLE 2.24. Peroxides of Aldehydes and Ketones

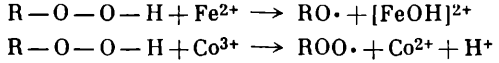
Formula	Name	m. p., °C	b. p., °C	Density d_4^{20}
Peroxides of aldehydes or dihydroxy peroxides				
$HOCH_2-OO-CH_2OH$	Formaldehyde peroxide	51	—	—
$HOCH(CH_3)-OO-CH(CH_3)OH$	Acetaldehyde peroxide	100	—	—
$HOCH(CCl_3)-OO-CH(CCl_3)OH$	Chloral peroxide	122	—	—
Peroxides of aldehydes and ketones or diperoxides				
	Acetone diperoxide	70°C (subl.)	—	—
	Diperoxide of methyl ethyl ketone	100 (expl.)	—	1.042 (at 15°C)
	Acetaldehyde diperoxide	63 (expl.)	—	—
Ozonides				
	Ethylene ozonide	—	18 (at 16 mm Hg)	1.265
	Pseudobutylene ozonide	—	27 (at 60 mm Hg)	1.027

find wide use as initiators of chain reactions. This action is based on the homolytic decomposition of peroxides which yields free radicals:

$$(CH_3)_3C-O-O-C(CH_3)_3 \longrightarrow 2(CH_3)_3CO\cdot$$
$$(CH_3)_3CO\cdot \longrightarrow (CH_3)_2C=O+CH_3\cdot$$



The decomposition of peroxides with the formation of radicals takes place not only as the result of thermal decomposition at not too high temperatures (below 100°C) but also because of the action (especially on hydroperoxides) of the cations of transition metals—oxidizing and reducing agents. For example,

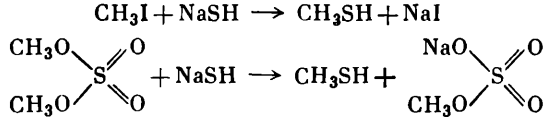


Thus, peroxides (on gentle heating) and hydroperoxides (in the presence of the cations of the metals Cr, Mn, Fe, Co, etc.) serve as initiators of chain homolytic reactions. For more detail, see Volume IV, "Free Radicals".

2.12. Sulphur Compounds

A. Thioalcohols (Mercaptans)

Hydrogen sulphide is the analogue of water. The alkylation of the acid salts of hydrogen sulphide leads to the formation of sulphur analogues of alcohols, RSH, which are called **thioalcohols, mercaptans** or **thiols**:



Mercaptans have an extremely nauseous smell. Methyl mercaptan, CH_3SH, is a gas, and those beginning with ethyl mercaptan, C_2H_5SH, are all liquids (Table 2.25). In distinction to water and alcohols, mercaptans are unassociated, like hydrogen sulphide, and therefore boil at much lower temperatures than the corresponding alcohols:

	b.p., °C		b.p., °C
CH_3OH	64.7	CH_3SH	7.6
C_2H_5OH	78.5	C_2H_5SH	34.7

According to the Geneva nomenclature, the ending for the names of this class of compounds ("thiol") is added to the name of the corresponding hydrocarbon: methanethiol, CH_3SH; ethanethiol, C_2H_5SH; 2-propanethiol, $CH_3—CH(SH)—CH_3$.

TABLE 2.25. **Thioalcohols or Mercaptans**

Formula	Name	m.p., °C	b.p., °C	Density d_4^{20}	Refractive index n_D^{20}	Dipole moment in benzene at 20°C, D
CH_3SH	Methyl mercaptan	—123.1	7.6	0.868	—	1.26
C_2H_5SH	Ethyl mercaptan	—121	34.7	0.840	1.4305	1.38 (at 15°C)
$CH_3CH_2CH_2SH$	*n*-Propyl mercaptan	—111.5	68	0.836	1.4380	1.33
$(CH_3)_2CHSH$	Isopropyl mercaptan	—130.7	60	0.816	1.4255	—
$CH_3(CH_2)_3SH$	*n*-Butyl mercaptan	—115.9	98	0.838	1.4440	1.32
$(CH_3)_2CHCH_2SH$	Isobutyl mercaptan	<-79	88	0.836	1.4386	—
$CH_3(CH_2)_4SH$	*n*-Amyl mercaptan	—75.7	126 (at 460 mm Hg)	0.857	1.4467	1.50 (at 25°C)
$(CH_3)_2CH(CH_2)_2SH$	Isoamyl mercaptan	—169	119	0.835	1.4412	—

Mercaptans exhibit weak acidic properties and when acted on by alkali they give salts called **mercaptides**:

$$RSH + NaOH \longrightarrow RSNa + H_2O$$

Mercaptans, however, are even weaker acids than hydrogen sulphide (the $+I$ effect of the alkyl group): the pK_a of ethyl mercaptan in water is 10.9 and that of hydrogen sulphide, 7.02. With heavy metals, which form insoluble sulphides, mercaptans also give precipitates of insoluble mercaptides. Such are, for example, insoluble colourless (in contrast to the coloured mercuric sulphide) mercuric mercaptides, $(RS)_2Hg$. In contrast to alcohols, mercaptans are easily oxidized. They can be titrated quantitatively with iodine; this results in dialkyl disulphides:

$$2RSH + I_2 \longrightarrow R{-}S{-}S{-}R + 2HI$$

which are also formed when mercaptans are slowly oxidized by atmospheric oxygen. Dialkyl disulphides are easily reduced, being again converted into mercaptans.

B. Thioethers (Dialkyl Sulphides)

The alkylation of a neutral salt of hydrogen sulphide or an alkali metal mercaptide leads to the formation of sulphur analogues of ethers—**thioethers** or **dialkyl sulphides** (Table 2.26):

$$2CH_3I + Na_2S \longrightarrow (CH_3)_2S + 2NaI \quad (1)$$

$$RI + RSNa \longrightarrow RSR + Na_2S \quad (2)$$

There also exist mixed thioethers, R—S—R′, which are produced by reaction (2) through the use of reagents containing different radicals.

Thioethers, like their oxygen analogues, are unassociated and boil at higher temperatures than ethers:

	b.p., °C		b.p., °C
$(CH_3)_2O$	−23.7	$(CH_3)_2S$	38
$(C_2H_5)_2O$	34.6	$(C_2H_5)_2S$	92

Dialkyl sulphides do not react with acids—they practically have no basic (protophilic) properties. It is interesting, however, to note that they form very stable complex compounds with a number of metal salts, say, $R_2S \cdot HgCl_2$, $R_2S \cdot AuCl_3$. The nucleophilic properties of dialkyl sulphides are also manifested in their reactions with alkyl halides, with which they form **sulphonium salts** (they do so especially readily with methyl iodide):

$$R_2S + RI \longrightarrow R_3S^+ I^-$$

TABLE 2.26. **Thioethers or Dialkyl Sulphides (Normal Structure)**

Formula	Name	m.p., °C	b.p., °C	Density d_4^{20}	Refractive index n_D^{20}	Dipole moment in benzene at 20°C, D
$(CH_3)_2S$	Dimethyl sulphide	−83.2	38.0	0.848	1.4355	1.40
$(C_2H_5)_2S$	Diethyl sulphide	−102.1	92.0	0.837	1.4430	1.58
$(C_3H_7)_2S$	Dipropyl sulphide	−101.9	142.0	0.814 (at 17°C)	—	1.55
$(C_4H_9)_2S$	Dibutyl sulphide	−79.7	185.0	0.838	1.4530	1.57
$(C_5H_{11})_2S$	Diamyl sulphide	−51.3	230	0.843	1.4556	1.58 (at 25°C)
$(C_7H_{15})_2S$	Diheptyl sulphide	—	298.0	0.842	1.4606	—

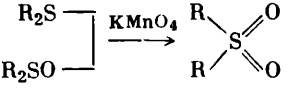
The cation R_3S^+ includes a tri-covalent positively charged (formally tetravalent) sulphur. These long-known tertiary sulphonium salts are the analogues of the tertiary oxonium salts, $R_3O^+BF_4^-$, described by Meerwein in 1937 (see page 162). Tertiary oxonium salts are less stable than sulphonium salts and are formed only with the anions of strong complex acids, but at the same time there are secondary oxonium salts, $[R_2O^+H]X^-$, which have no sulphonium analogues. The last example shows that nucleophilicity does not always parallel basicity.

C. Sulphoxides and Sulphones

Dialkyl sulphides are oxidized by hydrogen peroxide to **sulphoxides**:

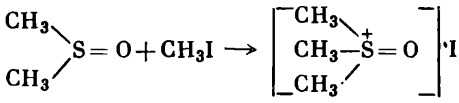
$$R_2S + H_2O_2 \longrightarrow R_2SO + H_2O$$

When subjected to more vigorous oxidation (with permanganate or concentrated nitric acid) dialkyl sulphides and also sulphoxides pass into **sulphones**:

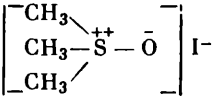


As has recently been established, sulphoxides react with methyl iodide in the same way as sulphides do, with the formation of onium

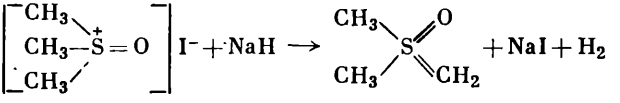
compounds of a new type—**sulphoxonium salts** (R. Kuhn):



As always, the S=O bond is close to a semi-polar bond, so that the formula of a sulphoxonium salt may also be written thus:



With sodium hydride, NaH, which acts like a strong alkali, this salt reacts with loss of HI and formation of a new interesting compound:



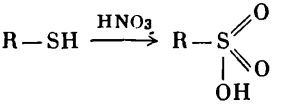
This compound is, as it were, a sulphone in which one oxygen has been replaced by CH_2.

Sulphones are neutral, crystalline and very stable compounds which are extremely difficult to reduce.

Dimethyl sulphoxide, $(CH_3)_2S{=}O$, is noted for a very high dielectric constant. At present it is widely employed in research work as a solvent, in which ordinarily non-ionizing substances undergo dissociation, such as alkyl halides or compounds with a protonated H—C bond.

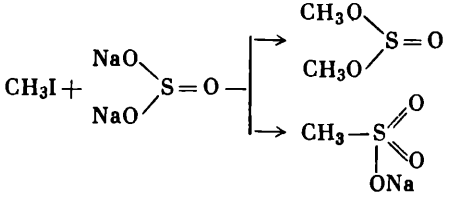
D. Alkanesulphonic Acids

The vigorous oxidation of mercaptans (and disulphides) leads to the formation of alkanesulphonic acids:

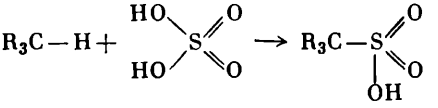


They can also be made by alkylation of sodium sulphite, the ordinary reaction of formation of sulphurous ester (alkylation at oxygen)

being accompanied by the centre-transfer reaction (see Volume II)—alkylation at sulphur:



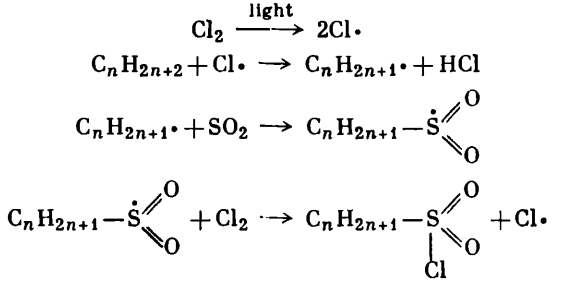
Hydrocarbons that contain a tertiary hydrogen atom are sulphonated under the action of fuming sulphuric acid to alkanesulphonic acids:



The sulphonation of hydrocarbons, which is of great importance in the aromatic series, is not practically used for preparing fatty sulphonic acids.

A different method for producing sulphonic acids was introduced in 1936—via their acid chlorides (sulphochlorides, RSO_2Cl).

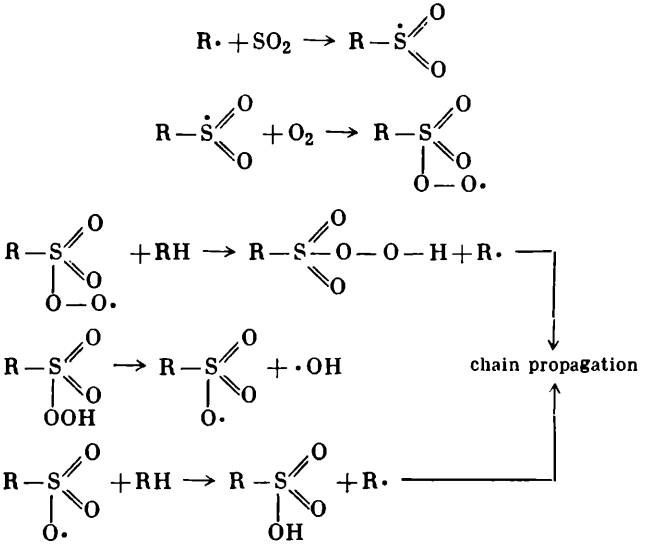
For example, the higher alkanes are reacted with chlorine and sulphur dioxide and the reaction is initiated by light. A chain reaction is developed:



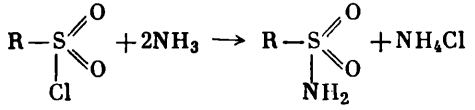
In this process, each hydrocarbon gives a mixture of isomeric acid chlorides since atomic chlorine pulls the hydrogen atom away from any link in the hydrocarbon. The chlorides of sulphonic acids are converted into sodium salts which are used as detergents and emulsifying agents suitable for application, for example, in hard and salty water.

An analogous process can also be carried out in the presence of oxygen, any source of free radicals being used to initiate a chain reaction; peroxides, for example, are added, which decompose to

give the radical R·:



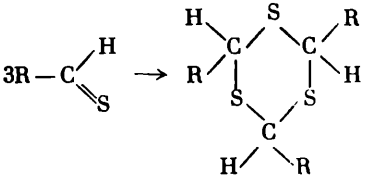
Alkanesulphonic acids are strong monobasic acids which form water-soluble salts of alkaline-earth metals and sparingly soluble sodium salts. With alcohols, these acids give esters, say, RSO_2OCH_3. The reaction with PCl_5 involves an ordinary replacement of the hydroxyl of the sulphoxyl group by the halogen with the formation of sulphonyl chlorides or sulphochlorides, RSO_2Cl, which are hydrolysed by water to the parent acids more slowly than carboxylic acid chlorides. When reacted with ammonia the acid chlorides form the amides of sulphonic acids (sulphamides):



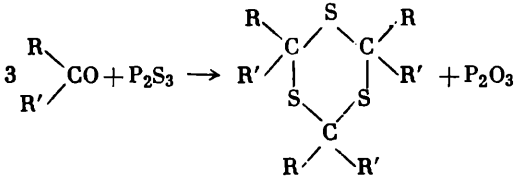
Sulphamides have no basic properties.

E. Thioaldehydes and Thioketones (Thials and Thions)

Thioaldehydes are rapidly converted into cyclic trimers:



which are made from aldehydes and ketones by the action of P_2S_3:

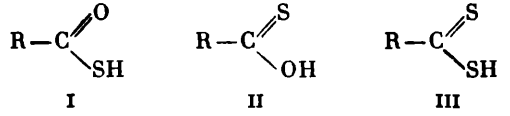


Monomeric thioketones (alkanethions) are best prepared by the action of hydrogen sulphide on ketals in the presence of a small amount of zinc chloride or in a solution of glacial acetic acid.

Monomeric thioacetone, $CH_3—CS—CH_3$, is a red liquid (b.p. 80°C) which has an extremely vile odour, said to be much worse than that of most other organosulphur compounds. It can be stored only for several hours since it polymerizes spontaneously. Thions are hydrolysed by water to ketones; with hydrazine, semicarbazide, etc., they react like ketones but more readily. The action of hydrogen sulphide on ketones in acid medium yields mainly 1,1-dithiols; for example, from acetone there is obtained the compound $CH_3—C(SH)_2—CH_3$. In contrast to two hydroxyls, two thiol groups remain attached to one carbon atom, and dithiols are not liable to be converted into thioketones.

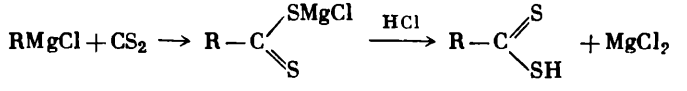
F. Thiocarboxylic Acids

The thiocarboxylic acids (thio acids) known at present are the following: thiolic acids (I), thionic acids (II) isomeric to thiolic acids, and dithio or dithionic acids (III):



I II III

Dithio acids can be made by the action of hydrogen sulphide on a Grignard reagent:



2.13. Nitrogen Derivatives of Alkanes

A. Nitroso Compounds

When primary amines, RNH_2 (page 282), were oxidized with a solution of a salt of peracetic acid (page 258)

$$CH_3-\overset{\overset{O}{\|}}{C}-O-ONa$$

in methylene chloride by Emmons in 1957, he succeeded in obtaining a number of aliphatic nitroso compounds of the general formula R—N=O with primary and secondary hydrocarbon radicals and also the well-known nitroso compounds with a tertiary radical.

An alternative method of preparing such compounds (Kharasch) is the reaction between free radicals and nitrogen oxide or an ester of nitrous acid. The decomposition of acetyl peroxide

$$CH_3\overset{\overset{O}{\|}}{C}-O-O-\overset{\overset{O}{\|}}{C}CH_3$$

in *sec*-butyl ester of nitrous acid (page 148), which involves the generation of methyl radicals, can yield nitrosomethane.

The structure of nitroso compounds follows from their oxidation to nitro compounds and reduction to primary amines:

$$CH_3-N=O \xleftarrow{:\ddot{O}:\ (KMnO_4)} CH_3-N=O \xrightarrow{Sn;\ HCl} CH_3-N\begin{matrix}H\\H\end{matrix} + H_2O$$

Nitroso compounds with primary and secondary hydrocarbon radicals are unstable and isomerize, especially in aqueous solutions, to form aldoximes and ketoximes:

$$R-CH_2-N=O \rightarrow R\diagdown\!\!\diagup C=N-OH \quad (H)$$

An aldoxime

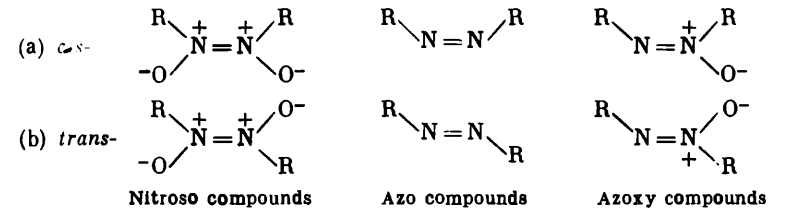
$$R\diagdown\!\!\diagup CH-N=O \rightarrow R\diagdown\!\!\diagup C=N-OH \quad (R')$$

A ketoxime

Thus, the nitroso group has an activating effect on the alpha-hydrogen atom and is similar in this respect to the carbonyl and nitro groups. Nitroso compounds are coloured blue-green. This absorption of light depends on the excitation of one of the electrons of the unshared electron pair on nitrogen (the so-called $n \rightarrow \pi^*$ transition; see Volume III). Blue-green nitroso compounds exist,

however, only in the liquid (in a solution, for example) and in the gas phase. When being converted to the solid state they undergo dimerization and become colourless; in solution they again dissociate, the dissociation following the usual laws of equilibrium.

Of the numerous formulas suggested for dimers the one analogous to the formulas of azo and azoxy compounds (see Volume III, "Azoxybenzene") should be considered here. The best argument in favour of the structure chosen is the existence of the recently discovered geometrical isomerism of nitroso compounds:



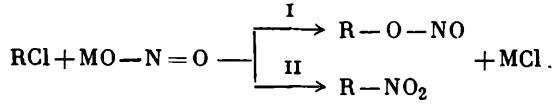
This type of geometrical isomerism—the existence of two different substances of the same structure but different configuration—is observed in compounds containing a double nitrogen-nitrogen or nitrogen-carbon bond and in unsaturated compounds with a double carbon-carbon bond (page 333). Two different configurations are possible for such compounds, just as in the examples given.

Stereoisomeric forms of aliphatic nitroso compounds differ, in particular, in infrared spectra. *Trans*-isomers are characterized by a single absorption band in the region of 1171-1290 cm^{-1}, and *cis*-isomers by two bands at 1323-1344 cm^{-1} and 1330-1420 cm^{-1}.

The most striking feature of dimers is however the ease of their dissociation, which has hardly any analogy among similar structures.

B. Nitro Compounds

The alkylation of salts of nitrous acid by alkyl halides involves two competing reactions. The preponderance of one of these reactions depends largely not so much on the conditions as on the nature of the alkyl and metal of the nitrite. The first normal route gives an ester of nitrous acid, and the second pathway which proceeds via a reaction-centre transfer (see Vol. II) leads to the formation of an isomeric nitro compound in which nitrogen is united directly to carbon:



A proof of the different bond orders for the atoms in the two isomers is provided by reduction reactions. On reduction nitrous acid esters yield an alcohol and hydroxylamine and nitro compounds are converted to amines:

$$R-ONO \xrightarrow{H_2} R-OH + \begin{matrix} H \\ \diagdown \\ N-OH \\ \diagup \\ H \end{matrix}$$

$$R-NO_2 \xrightarrow{H_2} R-N\begin{matrix} \diagup H \\ \\ \diagdown H \end{matrix} + 2H_2O$$

When the sodium salt of monochloroacetic acid is reacted with sodium nitrite, the reaction almost entirely takes the second route, i.e., a nitro compound is obtained:

$$ClCH_2-\underset{\underset{O}{\|}}{C}-ONa + NaNO_2 \longrightarrow O_2N-CH_2-\underset{\underset{O}{\|}}{C}-ONa + NaCl$$

The resulting sodium salt of nitroacetic acid probably rearranges first to an *aci*-form (see below) and is then decarboxylated. This may be depicted in a simplified way as follows:

$$O_2N-CH_2-\underset{\underset{O}{\|}}{C}-OH \longrightarrow O_2N-CH_3 + CO_2$$

This process is the usual method for preparing nitromethane in the laboratory (the Kolbe synthesis).

M. I. Konovalov discovered a reaction of direct nitration of hydrocarbons of the aliphatic series by dilute nitric acid at a temperature of 150°C. In this way, tertiary hydrogens can easily be replaced by the nitro group:

$$\begin{matrix} CH_3 \\ \diagdown \\ CH_3-C-H \\ \diagup \\ CH_3 \end{matrix} + HO-NO_2 \longrightarrow \begin{matrix} CH_3 \\ \diagdown \\ CH_3-C-NO_2 \\ \diagup \\ CH_3 \end{matrix} + H_2O$$

Secondary hydrogens are replaced with difficulty and primary hydrogens are not replaced at all (under the conditions indicated).

The above equation, however, is only the stoichiometric result of the reaction.

A. V. Topchiev and A. N. Titov have thoroughly studied the reaction of nitration in the aliphatic series and established its homolytic chain character. It can be accomplished not only with nitric acid

but also with the aid of nitrogen dioxide. Nitrogen dioxide which has an unpaired electron initiates a reaction chain:

$$HNO_3 \xrightarrow{t^\circ} HO\cdot + \cdot NO_2$$
$$RH + \cdot OH \longrightarrow R\cdot + H_2O$$
$$R\cdot + \cdot NO_2 \longrightarrow R{-}NO_2$$
$$R\cdot + HNO_3 \longrightarrow R{-}NO_2 + \cdot OH$$

A somewhat different process is used industrially at present, which makes it possible to prepare nitro compounds even from the most inert hydrocarbons—methane and ethane. The nitration is carried out at about 400°C by concentrated nitric acid, i.e., in the presence of nitrogen oxides.

Under these severe conditions, apart from the normal nitration reactions

$$CH_4 + HNO_3 \longrightarrow CH_3NO_2 + H_2O$$
$$CH_3{-}CH_3 + HNO_3 \longrightarrow CH_3CH_2NO_2 + H_2O$$
$$CH_3{-}CH_2{-}CH_3 + HNO_3 \longrightarrow \begin{cases} CH_3{-}\underset{\displaystyle NO_2}{\underset{|}{CH}}{-}CH_3 \\ CH_3{-}CH_2{-}CH_2NO_2 \end{cases}$$

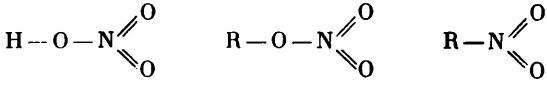
there also take place the reactions of destructive nitration (involving the cracking of hydrocarbon chains), as a result of which lower nitro compounds are also formed:

$$CH_3{-}CH_3 + 2HNO_3 \longrightarrow 2CH_3NO_2$$
$$CH_3{-}CH_2{-}CH_3 + 2HNO_3 \longrightarrow CH_3NO_2 + C_2H_5NO_2$$

The nitration of chloroform and chlorination of nitromethane can give trichloronitromethane, Cl_3CNO_2, which is usually called **chloropicrin**. This poisonous, tear gas is prepared industrially in a different way. Chloropicrin finds limited use as a fumigant (for destroying warehouse insects).

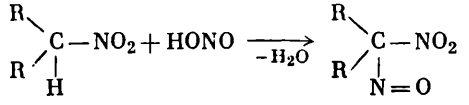
(a) *Structure of Nitro Compounds*

For a long time chemists made use of the formulas of nitric acid, nitrates and nitro compounds with pentacovalent nitrogen:

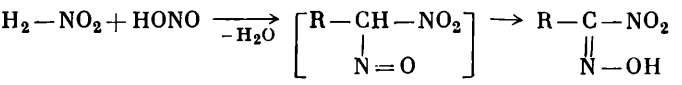


This representation is incorrect because nitrogen, an element of the second period (Li-Ne), may have no more than eight outer electrons around itself, whereas five covalent bonds correspond to

The mobility of the hydrogens of primary and secondary nitro compounds affects their behaviour towards nitrous acid. These reactions are absolutely analogous to the reactions of ketones with nitrous acid (page 185). In the case of secondary nitro compounds, their sole alpha-hydrogen is replaced by a nitroso group and the reaction of nitrosation ends up with the formation of **pseudo-nitrols**, which are to be regarded as nitro-nitroso compounds:



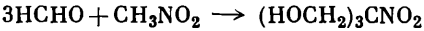
With a primary nitro compound, the transiently formed nitro-nitroso compound (pseudo-nitrol) isomerizes due to the strongly increased mobility of the hydrogen (just as in the case of ketones) with the transfer of the α-hydrogen (proton) to the nitroso group, which is thus converted to an oxime group. As a result, a weak **alkylnitrolic acid** is obtained:



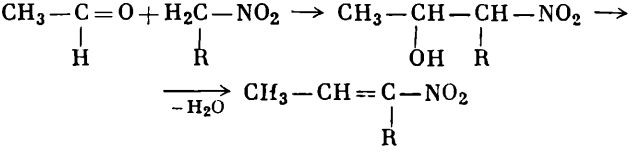
That the proton is transferred to the nitroso and not to the nitro group is understandable: the reaction proceeds with the formation of the least dissociated compound—the weakest **alkylnitrolic acid.**

Nitroparaffins are similar to carbonyl compounds also in their behaviour towards aldehydes.

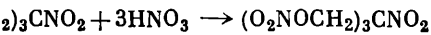
In a weakly alkaline solution, nitro compounds enter into condensation reactions with aldehydes and ketones (Henri). Nitromethane is condensed with formaldehyde according to the following scheme:



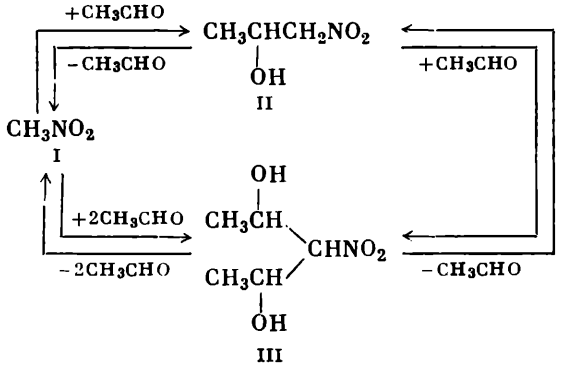
This reaction resembles the condensation of acetaldehyde with formaldehyde.* Condensations with other carbonyl compounds are similar to the aldol- and croton-type condensations and lead to unsaturated nitro compounds:



* Just as pentaerythritol synthesized from acetaldehyde (page 143), the product of condensation of nitromethane with formaldehyde is subjected to esterification with nitric acid to obtain an explosive compound:

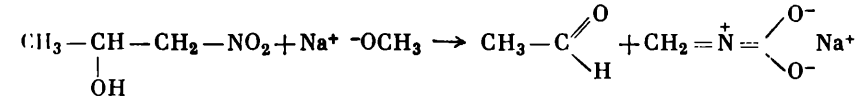


These condensations are typical examples of acid-base catalysis. According to the data obtained by Urbansky, the relations observed in the case of an aldol-type condensation are expressed by the following scheme:



(Under more drastic conditions, the water is lost and the "croton" stage of the condensation takes place.)

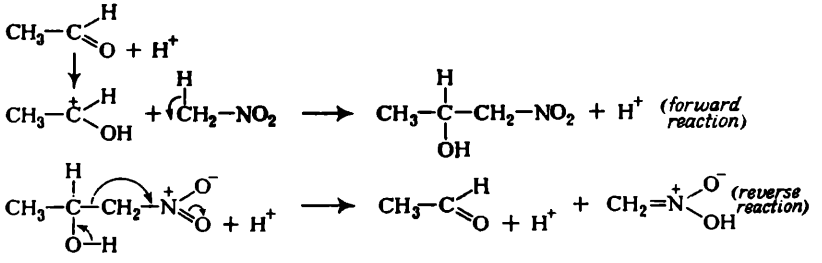
Very interesting is the reversibility of the aldol stage. For example, the action of sodium methylate can be used to decompose the condensation product II into acetaldehyde and a sodium salt of *aci*-nitromethane:



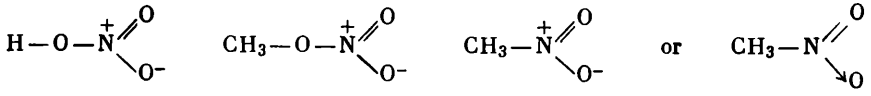
The splitting-off of one molecule of the aldehyde from compound III occurs even in a weakly alkaline medium (pH 7.5-8.5).

The catalytic role of an acid (H^+) and a base (^-OH) in a condensation reaction and in the reverse reaction can be explained with the aid of the schemes given below.

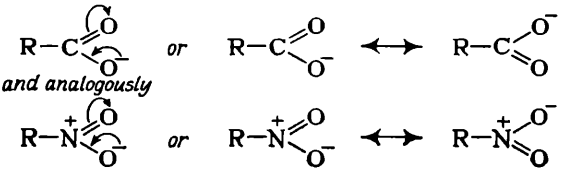
(a) The action of an acid:



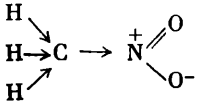
ten electrons. Therefore it would be more correct to write the formulas of the above compounds as follows:



that is, to represent one of the bonds between nitrogen and oxygen as a double bond and the other as a semipolar bond (page 30). In fact, however, both oxygen atoms are bound to nitrogen identically, the distance between each of the oxygen atoms and nitrogen is the same, and the two oxygen atoms have each a half negative charge. This is a case of mesomerism (or conjugation): the electron density becomes equilibrated just as in the carboxylate ion (page 236):



Since the nitrogen in nitro compounds carries a full positive charge and the two oxygens carry a negative charge, these compounds are polar solvents. The presence of a full positive charge on the key atom is responsible for the fact that the nitro group



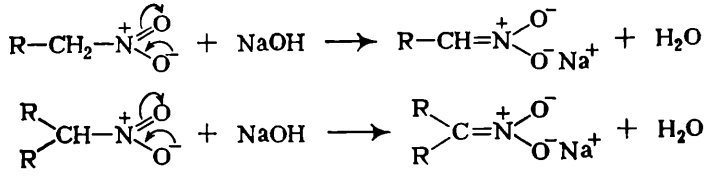
is the strongest electron-attracting group, which exhibits a $-I$ effect (page 246).

But the nitro group shows not only the $-I$ effect, which is ascribed to the full positive charge on nitrogen. It is also characterized, just as the carbonyl group, by the $-T$ effect which is very strongly pronounced and is reflected in the tautomerism of nitro compounds:

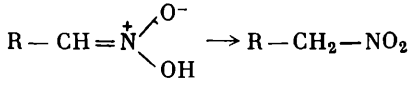
and also in all condensation reactions due to the presence of α-hydrogen atoms.

(b) *Properties of Nitro Compounds*

Because of the strongest electron-attracting properties of the nitro group the methyl group of nitromethane and, in general, the α-methylenic linkage of nitroalkanes have even more mobile (active) hydrogens than aldehydes and ketones. This reveals itself mainly in the fact that primary and secondary nitro compounds, i.e., compounds with a nitro group at a primary or secondary carbon ($R—CH_2—NO_2$ or $R_2CH—NO_2$), react with alkali, giving up a proton. In this process, the electron pair that bound the carbon to the now removed proton is migrating, thereby forming a bond between carbon and nitrogen. As a result, the charge of the anion becomes concentrated on the oxygen atom and salts of so-called *aci*-nitro compounds are formed:



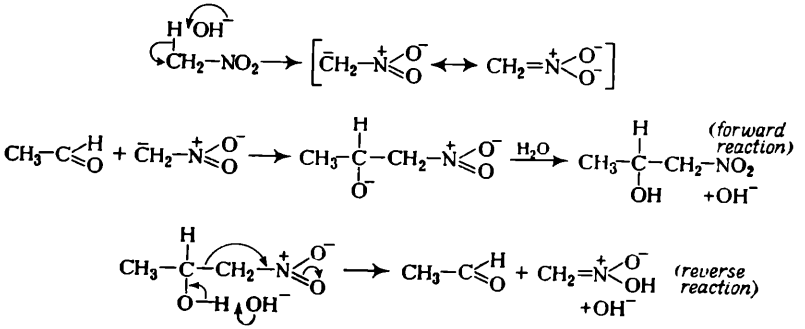
In certain cases (nitrotoluene, see Volume III) the oxidation of such salts yields an unstable isomer of the nitro compounds involved (called the *aci*-form); the *aci*-form usually isomerizes immediately to the more stable parent nitro form:



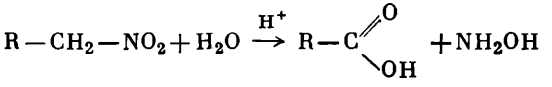
If this reaction is reversible, in which case the single arrow is replaced by the reversibility sign (⇌), this is known as the phenomenon of **tautomerism** (for more detail, see Vol. II), which in this case is called the nitro-*aci*-nitro tautomerism. In contrast to very weakly electrolytically dissociating nitro compounds, their isomers—*aci*-nitro compounds—are rather strong acids. The equilibrium is therefore found to be invariably shifted to the side of slightly dissociated true nitro compounds. For example, for nitromethane in water at 20°C the constant of tautomeric equilibrium $K_t = 10^{-17}$

The relation of nitro compounds to the salts of *aci*-nitro compounds is an example of what Hantzsch called the relation of a pseudo-acid (a nitro compound in this case) to its salt. A pseudo-acid is practically a neutral compound which reacts with alkali to form a salt (and water). The salt, however, has a different structure corresponding to the structure of an isomeric acid (a true acid), which is an *aci*-nitro form in this particular case.

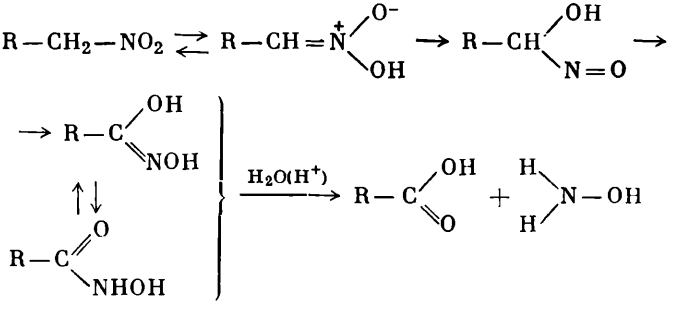
(b) The action of a base:



Under the action of concentrated acids, primary nitro compounds are hydrolysed, forming carboxylic acids and hydroxylamine:

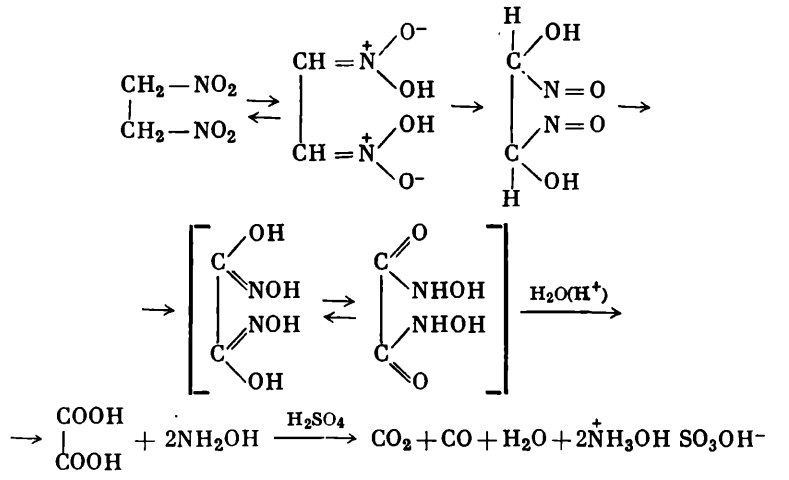


This reaction, which was discovered by Bamberger, proceeds through the stage of isomerization of an *aci*-nitro compound to a hydroxamic acid which undergoes hydrolysis to give hydroxylamine and a carboxylic acid:



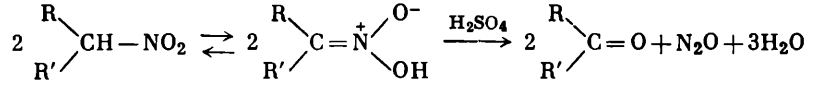
The Bamberger reaction is also employed industrially for synthesis of hydroxylamine. According to Urbansky it is expedient to make use of 1,2-dinitroethane for this purpose. In this case, the dinitroethane obtained from ethylene and NO_2 by the Demyanov

method (page 339) is acted on by concentrated sulphuric acid at 100°C:



In this way, pure hydroxylamine sulphate is produced.

When heated in aqueous solution with acids, primary and secondary nitro compounds are converted into aldehydes and ketones, respectively (Nef):



Tertiary nitro compounds react neither with alkalis nor with nitrous acid nor with aldehydes.

C. Polynitro Compounds

Of the compounds containing several nitro groups, mention should first be made of **tetranitromethane**, $C(NO_2)_4$, which is obtained by the action of concentrated nitric acid on a number of organic compounds, say, on acetic anhydride, $(CH_3CO)_2O$.

Tetranitromethane is a colourless liquid (b.p. 126°C). With hydrocarbons and other organic substances it forms extremely explosive mixtures. Tetranitromethane is used as a nitrating agent (Urbansky) since it readily loses its fourth nitro group which is replaced by hydrogen. This gives trinitromethane which is called **nitroform**, $CH(NO_2)_3$. This is a strong acid (three nitro groups exert very

strong inductive and tautomeric effect). Tetranitromethane reacts with olefins to form complex compounds which have a yellow colour (the Ostromyslensky test for the detection of an ethylenic double bond).

D. Saturated Amines

The products resulting from the replacement of the hydrogen atoms in ammonia by hydrocarbon groups are known as **amines** or **amine bases.**

In contrast to alcohols, nitro compounds and all the functions so far considered in this book, primary amines are compounds obtained by the replacement of one hydrogen atom in ammonia (RNH_2), no matter whether R is a primary, secondary or tertiary radical. The formula of secondary amines is R_2NH, and that of tertiary amines, R_3N. The name of an amine is generally obtained by adding the suffix *-amine* to the name of the hydrocarbon radical involved: CH_3NH_2—methylamine, $(CH_3)_2NH$—dimethylamine, $(CH_3)_3N$—trimethylamine, etc. According to the Geneva nomenclature, as always, the names of amines are formed from the name of a hydrocarbon with the longest chain, the name of a substituent amino group being added as a prefix: *amino* for NH_2, *methylamino* for $NHCH_3$, *dimethylamino* for $N(CH_3)_2$, etc. The position of the substituent (amino group) is defined by a numeral indicating the number of the carbon to which it is attached; for example,

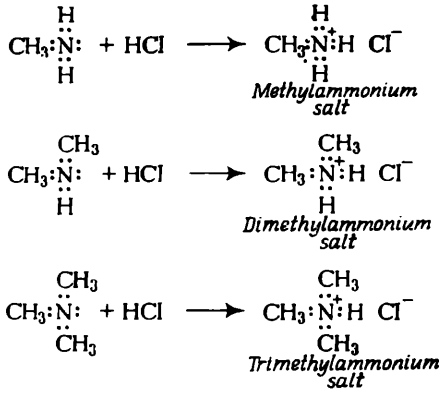
$$\begin{array}{l} CH_3-CH_2-\underset{\displaystyle NH_2}{\underset{|}{CH}}-CH_3 \end{array}$$

is called 2-aminobutane (also known as *sec*-butylamine). If the amino group is contained in a side chain, the prefix *amino* (or *alkylamino*, *dialkylamino*) is placed before the name of the radical making up the side chain.

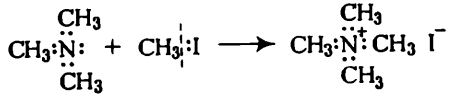
The simplest amines are gases readily soluble in water and having an odour resembling that of ammonia, but with a stronger "fishy" flavour to it. Trimethylamine has the smell of a herring. The physical properties of selected amines are given in Table 2.27.

Alkylamines are bases which are close in strength to ammonia, but usually somewhat stronger (due to the weak $+I$ effect of alkyl groups). The basic properties of amines, like those of ammonia, are due to the presence of an unshared electron pair on the nitrogen atom; this electron pair binds with the hydrogen ion of the acid as

a result of salt formation and gives alkylammonium salts:



In tertiary amines, the unshared electron pair on the nitrogen atom may be used also for the reaction with an alkyl halide (compare with sulphonium salts, page 266):



This results in the formation of a quaternary ammonium salt. Of course, there are amines and ammonium salts which contain different radicals.

(a) *Preparation of Amines*

1. The principal method is the alkylation of ammonia (or amines) with alkyl halides (the Hofmann reaction), dialkyl sulphates or tertiary oxonium salts. The reaction proceeds through the stage of addition of an alkyl group to the unshared electron pair on the nitrogen atom, followed by the removal of hydrogen halide by excess ammonia (or amine):

$$RI \xrightarrow{NH_3} R\overset{+}{N}H_3\ I^- \xrightarrow{NH_3} RNH_2 + NH_4I$$

$$RI \xrightarrow{RNH_2} R_2\overset{+}{N}H_2\ I^- \xrightarrow{NH_3} R_2NH + NH_4I$$

$$RI \xrightarrow{R_2NH} R_3\overset{+}{N}H\ I^- \xrightarrow{NH_3} R_3N + NH_4I$$

$$RI + R_3N \longrightarrow R_4\overset{+}{N}\ I^-$$

TABLE 2.27. **Amines**

Formula	Name	m.p., °C	b.p., °C	Density d_4^{20}	Refractive index n_D	Dipole moment in benzene at 25°C D
CH_3NH_2	Methylamine	—92.5	—6.5	0.769 (d_4^{-70})	1.432 (at 17.5°C)	1.46
$(CH_3)_2NH$	Dimethylamine	—96.0	7.4	0.680 (d_4^0)	1.350 (at 17.0°C)	1.17
$(CH_3)_3N$	Trimethylamine	—124.0	3.5	0.635	1.363 (at 0°C)	0.86
$CH_3CH_2NH_2$	Ethylamine	—80.6	16.6	0.683	1.366	1.28, 1.39
$(CH_3CH_2)_2NH$	Diethylamine	—50.0	55.5	0.7056	1.3873 (at 18°C)	1.20
$(CH_3CH_2)_3N$	Triethylamine	—114.8	89.5	0.727	1.403	0.90
$CH_3CH_2CH_2NH_2$	*n*-Propylamine	—83.0	48.7	0.719	1.3900 (at 16.6°C)	1.33 (at 20°C)
$(CH_3CH_2CH_2)_2NH$	Di-*n*-propylamine	—39.6	110.7	0.7384	1.4045 (at 19.5°C)	1.07 (at 20°C)
$(CH_3CH_2CH_2)_3N$	Tri-*n*-propylamine	—93.5	156.0	0.757	1.4176 (at 19.4°C)	0.74
$CH_3(CH_2)_3NH_2$	*n*-Butylamine	—50.5	77.8	0.740	1.4010 (at 20°C)	1.40
$CH_3(CH_2)_4NH_2$	*n*-Amylamine	—55.0	104.0	0.761	1.4118 (at 20°C)	1.55 (at 30°C)
$CH_3(CH_2)_5NH_2$	*n*-Hexylamine	—19.0	132.7	0.7660 (d_4^{20})	1.4180 (at 20°C)	1.59 (at 30°C)

In this reaction, the halide undergoes nucleophilic substitution by the nitrogen of ammonia or amines or, what is the same thing, the nitrogen is subjected to electrophilic attack by the alkyl.

Depending on the ratio of the reagents and the conditions of the Hofmann reaction, a mixture of the primary, secondary, and tertiary amines and a quaternary ammonium salt is obtained, the low- and high-alkylated products predominating.

2. The aliphatic amines were first discovered by Wurtz (1848) as the result of the hydrolysis of esters of isocyanic acid (isocyanates):

$$R-N=C=O+H_2O \longrightarrow RNH_2+CO_2$$

Isocyanates are obtained by alkylation of silver cyanate.

3. An important reaction for preparing amines, the last stage of which is the hydrolysis of isocyanates, is the Hofmann degradation of acid amides. When an acid amide is acted on by NaOCl or NaOBr, one hydrogen atom of the amino group is replaced by a halogen and the alkali removes hydrogen halide from the nitrogen:

$$R-\overset{\overset{O}{\|}}{C}-NH_2+NaOCl \longrightarrow R-\overset{\overset{O}{\|}}{C}-N\begin{matrix}H\\Cl\end{matrix}$$

$$R-\overset{\overset{O}{\|}}{C}-N\begin{matrix}H\\Cl\end{matrix} + NaOH \longrightarrow R-\overset{\overset{O}{\|}}{C}-N\begin{matrix}\diagup\\\diagdown\end{matrix} + NaCl + H_2O$$

The resulting molecule with the unsaturated nitrogen atom rearranges to an isocyanate:

$$R-\overset{\overset{O}{\|}}{C}-N\begin{matrix}\diagup\\\diagdown\end{matrix} \longrightarrow O=C=N-R$$

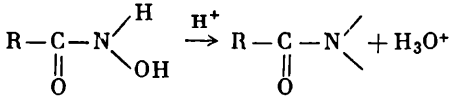
which is hydrolysed to a primary amine and carbon dioxide:

$$O=C=N-R+H_2O \longrightarrow RNH_2+CO_2$$

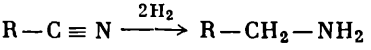
The same unstable molecule, which rearranges to an isocyanate and then gives a primary amine, is obtained by heating an acid hydrazide (Curtius):

$$R-\underset{\underset{O}{\|}}{C}-N=\overset{+}{N}=\overline{N} \longrightarrow R-\underset{\underset{O}{\|}}{C}-N\begin{matrix}\diagup\\\diagdown\end{matrix} + N_2$$

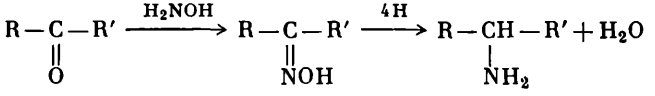
or by the action of acids on a hydroxamic acid (Lossen):



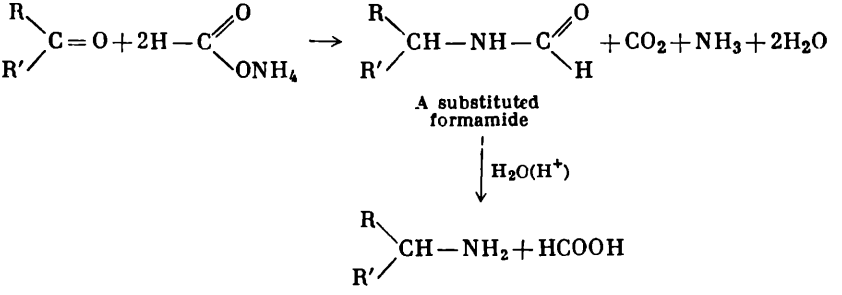
4. The reduction of nitriles (catalytic—with hydrogen over palladium or sodium in alcohol) gives primary amines:



5. Carbonyl compounds can be converted into any nitrogen functional derivative (an oxime or hydrazone) which may be reduced *in situ* to a primary amine:

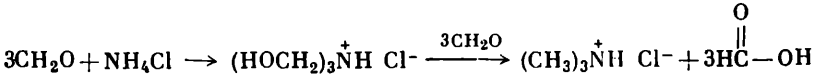


Another way of converting carbonyl compounds into amines consists in heating aldehydes and ketones with ammonium formate (the Leuckart reaction):



As can be seen from the above reactions, all the methods, except the Hofmann reaction, furnish primary amines only.

A specific method of preparing methylamines, in particular trimethylamine, is the interaction of paraform, which depolymerizes in the reaction to formaldehyde, with ammonium chloride. The initially formed methylol derivatives of ammonia are reduced by formaldehyde to amines:



(b) *Chemical Properties of Amines*

1. Amines as bases form salts even with very weak acids such as carbonic, hydrosulphuric and hydrocyanic acids; with water they give alkylammonium hydroxides:

$$CH_3NH_2 + HOH \longrightarrow CH_3\overset{+}{N}H_3\ OH^-$$

which show an alkaline reaction with ordinary indicators.

Like ammonia, amines form complex cations with a large variety of cations of heavy metals (Ag^+, Cu^{2+}, Co^{2+}, Co^{3+}, etc.).

Quaternary ammonium salts on replacement of their anion by OH^-, which is achieved, for example, through exchange with moist silver oxide, give the corresponding hydroxides:

$$2(CH_3)_4\overset{+}{N}\ Cl^- + Ag_2O + H_2O \longrightarrow 2(CH_3)_4\overset{+}{N}\ OH^- + 2AgCl$$

which are much stronger bases than water solutions of ammonia and amines. For example, tetramethylammonium hydroxide, $(CH_3)_4N^+\ OH^-$, is not inferior in basic properties to caustic alkalis since it is completely ionic.

2. Amines with hydrogen attached to nitrogen, i.e., primary and secondary amines, are acylated, just like ammonia, and by the same reagents (page 228), forming substituted **amides**:

$$CH_3-\overset{\overset{O}{\|}}{C}-Cl + 2C_2H_5NH_2 \longrightarrow \underset{\text{Ethylacetamide}}{CH_3-\overset{\overset{O}{\|}}{C}-NHC_2H_5} + C_2H_5\overset{+}{N}H_3\ Cl^-$$

$$CH_3-\overset{\overset{O}{\|}}{C}-Cl + 2(CH_3)_2NH \longrightarrow \underset{\text{Dimethylacetamide}}{CH_3-\overset{\overset{O}{\|}}{C}-N(CH_3)_2} + (CH_3)_2\overset{+}{N}H_2\ Cl^-$$

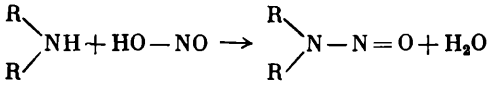
3. Primary amines react in a specific way with nitrous acid, being converted into alcohols:

$$R-NH_2 + HONO \longrightarrow \underset{\substack{\text{A primary}\\ \text{nitrosamine}}}{R-NH-N=O} \rightleftarrows \underset{\substack{\text{An alkyldiazo}\\ \text{hydrate}}}{R-N=NOH} \xrightarrow{HCl}$$

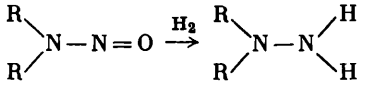
$$\longrightarrow \underset{\substack{\text{An alkyldiazonium}\\ \text{chloride}}}{R-\overset{+}{N}\equiv N\ Cl^-} \longrightarrow N_2 + Cl^- + R^+ \xrightarrow{H_2O} ROH + H^+$$

The intermediate compounds given are not isolated; they are written by analogy with similar aromatic compounds where they are well known (see Volume III).

Secondary amines are nitrosated by nitrous acid at the nitrogen being converted into **nitrosamines**:



A proof of this is furnished by the reduction of a nitrosamine to a disubstituted hydrazine:



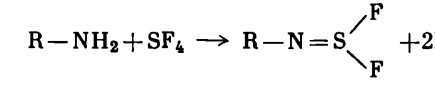
Tertiary amines do not react in this way with nitrous acid.

4. Primary amines when heated with chloroform in alcoholic alkali form **carbylamines**, which are often called **isonitriles** (page 291):

$$RNH_2 + CHCl_3 + 3NaOH \longrightarrow RNC + 3NaCl + 3H_2O$$

In contrast to nitriles, isonitriles are toxic and have a vile odour. The reaction of their formation is therefore a sensitive qualitative test for primary amines.

5. With sulphur tetrafluoride, primary amines react in a dual way (Kon and MacDiarmid):



(CH_3NSF_2 is a liquid with b.p. 16°C and m.p. −123°C)

$$2R-NH_2 + SF_4 \longrightarrow R-N=S=N-R + 4HF$$

Both types of compounds are capable of polymerization.

6. With thionyl chloride, $SOCl_2$, primary amines form sulphinimines, $R-N=S=O$ (more precisely, $R-N=S \rightarrow O$).

7. Tertiary amines when oxidized by H_2O_2 are converted into *tert*-amine oxides, in which the nitrogen and oxygen are linked to each other by a semipolar bond:

$$R_3N + H_2O_2 \longrightarrow R_3\overset{+}{N}-\bar{O} + H_2O$$

8. When methyl iodide is added to tertiary amines, the iodide ion in the quaternary salt being then exchanged for a hydroxyl, bases are obtained, which on pyrolysis decompose with loss of water and formation of a tertiary amine and an unsaturated hydrocarbon; for example,

$$(CH_3CH_2CH_2)_3\overset{+}{N}-CH_3\ OH^- \longrightarrow$$
$$\longrightarrow H_2O + (CH_3CH_2CH_2)_2N-CH_3 + CH_2=CH-CH_3$$

This reaction (called the Hofmann elimination) is of value for establishing the structure of nitrogen-containing heterocyclic compounds (see Volume III).

E. Diamines

Just as in the case of two hydroxyls, only in rare compounds [for example, in urea, $(NH_2)_2CO$] are two primary amino groups held by one carbon atom. Methylenediamine is very unstable. The simplest primary diamine—ethylenediamine (1,2-diaminoethane)—is obtained by ammonolysis of dichloroethane:

$$ClCH_2-CH_2Cl+4NH_3 \rightarrow H_2N-CH_2-CH_2-NH_2+2NH_4Cl$$

Its homologues with the amino group in the 1,2-position, say, 1,2-diaminopropane, can also be prepared by this method. The homologues with amino groups remote from one another can be synthesized by reduction of hydrazones or oximes of diketones:

$$CH_3-\underset{\underset{NOH}{\|}}{C}-CH_2-\underset{\underset{NOH}{\|}}{C}-CH_3 \xrightarrow{Na;\ C_2H_5OH} CH_3-\underset{\underset{NH_2}{|}}{CH}-CH_2-\underset{\underset{NH_2}{|}}{CH}-CH_3$$

or by reduction of dinitriles:

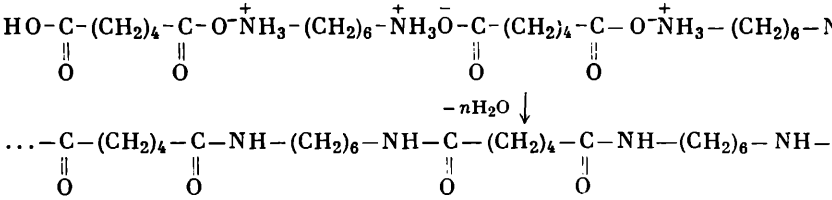
$$N\equiv C-(CH_2)_2-C\equiv N \xrightarrow{Na;\ C_2H_5OH} H_2N-CH_2-(CH_2)_2-CH_2-NH_2$$

$$N\equiv C-(CH_2)_4-C\equiv N \xrightarrow{H_2/Pd} H_2N-CH_2-(CH_2)_4-CH_2-NH_2$$

Dinitriles are made by dehydration of ammonium salts of dibasic acids.

The last reaction (the catalytic reduction of dinitriles) has become of great value. By this method, from adipic acid there is obtained hexamethylenediamine (or 1,6-diaminohexane)—an important product, which is subjected to polycondensation with adipic acid (or with its acid chloride) to give a high-molecular-weight polyamide (Nylon). The molten polymer is spun at 270-280°C into nylon fibre which is used for the manufacture of domestic (fabrics, women's hosiery) and technical items (various types of ropes). Polyamides are also used for the fabrication of strong films and tubings, particularly substitutes for blood vessels in surgery. The process used for preparing Nylon is basically the well-known reaction of conversion of an ammonium salt into a substituted amide by way of dehydration. Adipic acid and hexamethylenediamine first form a salt (called

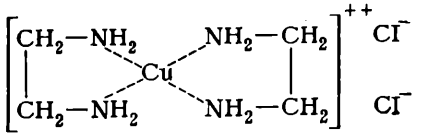
"nylon salt") which is then dehydrated by heating to form a poly mide:



The molten polyamide is forced through a spinneret containi fine jets and then the cooled fibre is wound up on bobbins whi stretch the fibre and thereby orient the macromolecules of polyamid parallel to each other, which considerably increases the streng of the fibre. Other types of polyamide fibres are described in Vc ume II.

It is because of this application that diamines have assumed co mercial importance. Formerly, only some of the natural diamin were known, say, putrescine, $NH_2-(CH_2)_4-NH_2$; and cadaverin $NH_2-(CH_2)_5-NH_2$.

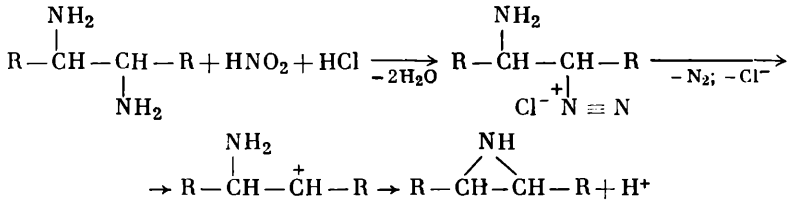
Ethylenediamine is used in investigations of inorganic compoun since it readily forms complex compounds with the same catio that give complex cations and with ammonia too. In contrast ammonia, ethylenediamine forms coordination compounds wi metals so that in the complexes obtained both nitrogen atoms a coordinated to the metal (they occupy two neighbouring coordir tion sites). For example, its complex with copper has the followi structure:



The reactions of diamines are similar to those of monoamin for example, they are converted into glycols by the action of nitr acid.

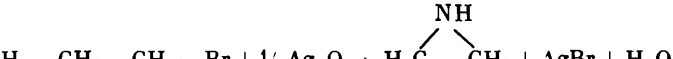
An interesting complication is observed if 1,2-diamine is lia to assuming a staggered conformation (see page 426) in which amino groups are most remote from each other. In this case, w nitrous acid attacks the first amino group and the nitrogen molec is ejected from the resulting unstable diazonium cation, the sec amino group is found to be contiguous, with its unshared elect

pair, to the bare carbonium ion, and a cyclic three-membered imine is formed:

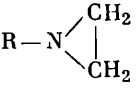


This course of the reaction is the effect of "participation of neighbouring groups in displacement reactions" or "anchimeric assistance" (Greek, *anchi*, near; *meros*, part)—an important phenomenon discovered by Winstein.

A nitrogen analogue of ethylene oxide—ethyleneimine (aziridine)—can be obtained by the reaction:



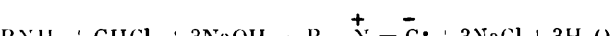
Like ethylene oxide, ethyleneimine is capable of opening its ring readily, but there is a difference between them since ethyleneimine forms, as a result of alkylation at the nitrogen, a number of derivatives of the type



The ethyleneimine grouping evidently exhibits *mutagenous properties*, i.e., is capable of attacking chromosomes.

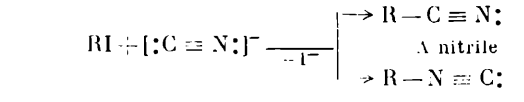
F. Isonitriles (Carbylamines)

The action of chloroform and alkali on primary amines produces **isonitriles** which are also known as **isocyanides or carbylamines:**



The reaction possibly proceeds through an intermediate stage at which dichlorocarbene, CCl_2 (page 107), is formed.

Carbylamines are isomeric to nitriles and may be regarded as the nitrogen-alkylated anion of hydrocyanic acid:



The anion of hydrocyanic acid is a so-called ambident ion, i.e., an anion in which the charge is shared between two atoms, in this case between carbon and nitrogen:

$$\bar{C} \equiv N:$$

On nucleophilic substitution this anion may attack either by its carbon atom (leading to nitriles) or by its nitrogen atom (with the formation of isonitriles). Usually, a mixture of nitriles and isonitriles results, though the nitriles predominate in the case of primary radicals and the isonitriles are exclusively formed in the case of tertiary radicals. Generally speaking, the direction of the reaction depends on the following factors: (a) the nature of the alkyl halide (as has already been stated); (b) the nature of the solvent; (c) the nature of the cation in the salt of hydrocyanic acid. The amount of the isonitrile increases when working in a protic polar solvent or if silver cyanide is used instead of sodium cyanide.

As seen, all the factors contributing to the mechanism of halogen substitution by the S_N1 route (see page 103 *et seq.*) favour the formation of isonitriles. In considering this and similar reactions, Kornblum deduced a rule: ambident anions react by the most nucleophilic portion under conditions favourable for the S_N2 mechanism and by the most negatively charged portion under the conditions of the S_N1 mechanism. The nitrogen in the cyanide anion should be looked upon as an atom richest with electrons.

The Kornblum rule extends to a number of other reactions, for example, the preparation of nitro compounds and nitrous acid esters from alkyl halides under the action of metal nitrites. The most nucleophilic centre in the anion of nitrous acid is the nitrogen atom, and the oxygen has the greatest electron density. As a result, the same factors that contribute to the formation of isonitriles favour in this case the formation of nitrous acid esters, and those factors which contribute to the formation of nitriles cause the formation of nitro compounds:

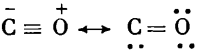
$$(CH_3)_3CX + AgONO \rightarrow (CH_3)_3CONO + AgX$$

$$RCH_2X + NaNO_2 \rightarrow RCH_2-N\begin{matrix}=O\\ \searrow O\end{matrix} + NaX$$

The best method of preparing isonitriles is the dehydration of alkyl formamides:

$$R-NH-C\begin{matrix}=O\\ \diagdown H\end{matrix} + P_2O_5 \rightarrow R-\overset{+}{N} \equiv \bar{C} + 2HPO_3$$

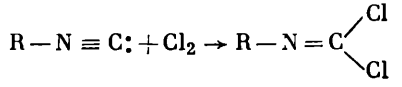
The structure of isonitriles (isocyanides) is similar to that of carbon monoxide:



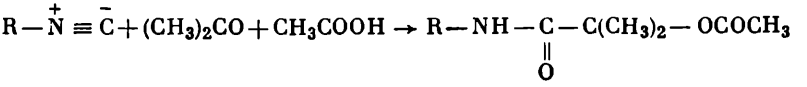
The formula with a triple bond, R—N≡C, reflects better the physical properties of isonitriles, which follows, for example, from the characteristic frequency of the N≡C bond in the infrared spectra:

	ν, cm^{-1}
C≡C bond	2140-2260
Isonitriles $R-\overset{+}{N}\equiv\overset{-}{C}$	2180-2120
Nitriles R—C≡N	2260-2240

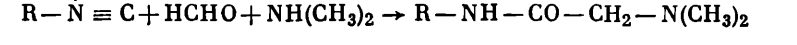
The unusual valence state of the carbon in isonitriles manifests itself in reactions of addition of the halogens, mercury salts, etc.:



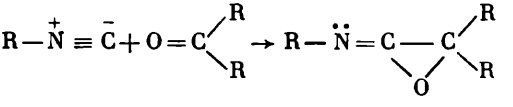
Isonitriles add carbonyl compounds and carboxylic acids (Passerini):

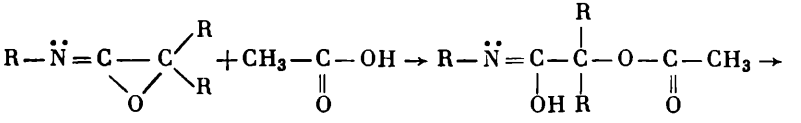


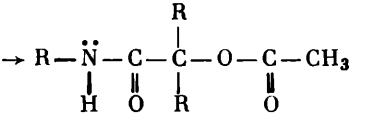
and also carbonyl compounds and amines:



The first stage of the reaction is presumably the addition of a carbonyl compound to an isonitrile with the subsequent opening of the three-membered heterocycle:







The difference from nitriles also shows up on hydrolysis. Isonitriles are hydrolysed only in acid medium:

$$R-\overset{+}{N}\equiv\overset{-}{C}+2H_2O \rightarrow H-C\begin{matrix}=O\\ \diagdown OH\end{matrix}+RNH_2$$

and nitriles are hydrolysed on boiling both with alkalis and acids:

$$R-C\equiv N:+2H_2O \rightarrow R-C\begin{matrix}=O\\ \diagdown OH\end{matrix}+NH_3$$

The hydrolysis of hydrocyanic acid corresponds to both reactions:

$$HCN+2H_2O \rightarrow HC\begin{matrix}=O\\ \diagdown OH\end{matrix}+NH_3$$

G. Aliphatic Diazo Compounds

Diazomethane was discovered by Pechmann in 1894 by means of the reaction between alkali and nitrosomethyl urethane (see below).

Attempting to accomplish the isonitrile synthesis with the aid of chloroform on the basis of hydrazine, Hermann Staudinger obtained diazomethane instead of the expected isonitrile $H_2N-\overset{+}{N}\equiv C$:

$$H_2N-NH_2+CHCl_3+3NaOH \rightarrow CH_2=\overset{+}{N}=\overset{-}{N}+3NaCl+3H_2O$$

Ordinarily, diazomethane which has become an important reagent is prepared by means of one of the following reactions:

$$CH_3-NH-\underset{\underset{O}{\|}}{C}-NH_2 \xrightarrow{HNO_2} CH_3-\underset{\underset{NO}{|}}{N}-\underset{\underset{O}{\|}}{C}-NH_2 \xrightarrow{2NaOH}$$

Methylurea — Nitrosomethylurea

$$\rightarrow CH_2=\overset{+}{N}=\overset{-}{N}+Na_2CO_3+NH_3+H_2O$$

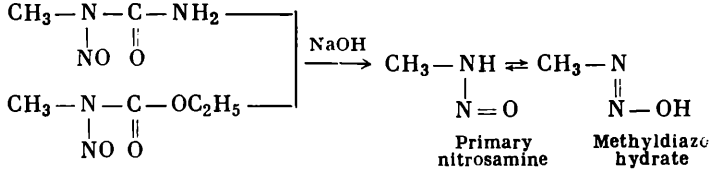
$$CH_3-NH-\underset{\underset{O}{\|}}{C}-OC_2H_5 \xrightarrow{HNO_2} CH_3-\underset{\underset{NO}{|}}{N}-\underset{\underset{O}{\|}}{C}-OC_2H_5 \xrightarrow{2NaOH}$$

Methyl urethane — Nitrosomethyl urethane

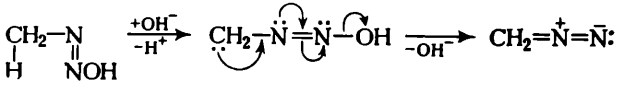
$$\rightarrow CH_2=\overset{+}{N}=\overset{-}{N}+Na_2CO_3+C_2H_5OH+H_2O$$

These reactions consist basically in the following: the nitrosated amide (or ester) when hydrolysed first forms a primary nitrosamine–

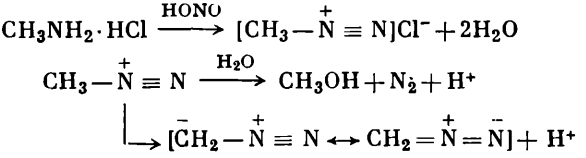
a tautomer of unstable methyldiazo hydrate (cf. an aromatic diazo hydrate, Volume III):



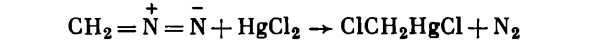
Possessing a very mobile hydrogen in its methyl group (the diazo group is an electron-withdrawing group), methyldiazo hydrate gives up a proton to alkali and changes into diazomethane:



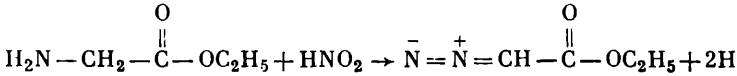
The direct diazotization of primary amines, as was indicated earlier for amines, leads to an alcohol with evolution of nitrogen. However, there are grounds for believing that this reaction proceeds through the stage of formation of an unstable diazonium cation:



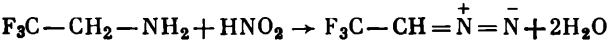
The possibility of the partial formation of diazomethane is evidenced by small amounts of chloromethylmercurichloride obtained when diazotization is carried out in the presence of $HgCl_2$ (A. N. Nesmeyanov). Chloromethylmercurichloride is made from diazomethane and $HgCl_2$ by the Hellermann reaction:



Diazoalkanes containing electron-attracting substituents in its methylene group ($-I$ effect) are more stable and can be prepared by direct diazotization of the corresponding amines. This method is employed to obtain, say, diazoacetic ester from a glycocoll ester:



Direct diazotization of trifluoroethylamine results in β,β,β-trifluorodiazoethane:



Diazomethane is a very toxic yellow-green gas (b.p. —24°C) soluble in ether. It is extremely reactive and reacts instantly with acids but is stable to the action of alkalis. The structure of diazomethane has been conclusively proved by electron diffraction measurements carried out on gaseous diazomethane (Bersh). The carbon atom and both nitrogen atoms lie on a single line; the C—N distance is 1.34 Å and the N=N distance is 1.13 Å, i.e., the C—N bond length is intermediate between the length of a single bond and that of a double bond, and the N=N bond length is intermediate between the length of a double bond and that of a triple bond. The structure of diazomethane may be represented as follows*:

$$\bar{C}H_2-\overset{+}{N}\equiv N: \leftrightarrow CH_2=\overset{+}{N}=\bar{N}:$$

The spreading of the negative charge between the extreme atoms lying on a straight line accounts for the relatively low dipole moment of the molecule, which is equal to 1.4 D.

The most significant reaction of aliphatic diazo compounds is the interaction with the hydrogen ion. In aqueous solution the reaction leads to an alcohol:

$$\bar{C}H_2-\overset{+}{N}\equiv N: + H^+ \rightarrow CH_3-\overset{+}{N}\equiv N: \rightarrow CH_3^{\oplus} + N_2$$
$$CH_3^{\ddagger} + H_2O \rightarrow CH_3OH + H^+$$

In the absence, or with a small concentration, of water the methyl cation attacks the acid anion and the methyl ester of the given acid is formed:

$$R-\underset{\underset{O}{\|}}{C}-OH + CH_2=\overset{+}{N}=\bar{N} \rightarrow R-\underset{\underset{O}{\|}}{C}-OCH_3 + N_2$$

This is an exceedingly convenient method for the conversion of acids into their methyl esters, the method being especially useful for work with small quantities of the compound.

With phenols diazomethane reacts in the same manner (see Volume III, "Phenols"):

$$\underset{\text{Phenol}}{C_6H_5OH} + CH_2=\overset{+}{N}=\bar{N} \rightarrow \underset{\substack{\text{Methylphenyl}\\ \text{ester}}}{C_6H_5OCH_3} + N_2$$

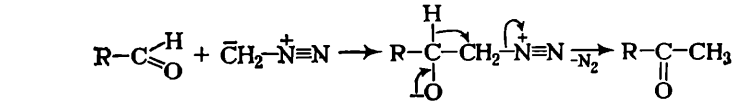
Alcohols can be methylated by diazomethane, for which purpose they are first converted into complex acids, which is accomplished

* In the following two reactions the free electron pairs on nitrogens are denoted by two dots for the sake of clarity; further in the text they are omitted and only the plus or minus sign is used. The minus on carbon indicates an unshared electron pair, and that on the nitrogen linked by a double bond, two unshared electron pairs.

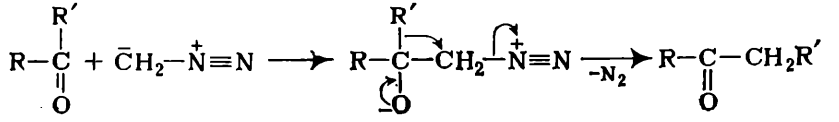
in practice by addition of small quantities of $ZnCl_2$ ($ZnCl_2$ is regenerated during the reaction) or other Lewis acids:

$$ROH + ZnCl_2 \rightarrow \underbrace{[ROZnCl_2]^-H^+ + CH_2{=}\overset{+}{N}{=}\overset{-}{N}}$$
$$\downarrow$$
$$ROCH_3 + N_2 + ZnCl_2$$

The reaction of diazomethane with aldehydes and ketones proceeds through its addition and hydride transfer. In this reaction, aldehydes are converted into methyl ketones:



The interaction with ketones involves the rearrangement of the skeleton: R′ migrates to CH_2 and a homologue of the starting ketone is obtained:



The reactions between diazomethane and the acid chlorides of inorganic and organic acids take place as follows:

$$AcCl + CH_2{=}\overset{+}{N}{=}\overset{-}{N} \rightarrow CH_2\begin{matrix}\diagup Cl \\ \diagdown Ac\end{matrix} + N_2$$

where Ac = acyl.

Thus, from acetyl chloride there can be obtained the ketone

$$CH_3{-}\overset{O}{\overset{\|}{C}}{-}CH_2{-}Cl$$

But if the reaction is conducted in excess diazomethane, the acetyl replaces the mobile hydrogen of the methylene group of diazomethane, a diazoketone is formed, and the hydrogen chloride evolved is bound by the excess diazomethane into methyl chloride:

$$CH_3{-}\overset{O}{\overset{\|}{C}}{-}Cl + 2CH_2{=}\overset{+}{N}{=}\overset{-}{N} \rightarrow \underset{\text{A diazoketone}}{CH_3{-}\overset{O}{\overset{\|}{C}}{-}CH{=}\overset{+}{N}{=}\overset{-}{N}} + CH_3Cl + N_2$$

By this method (the Arndt-Eistert reaction) diazoketones are prepared.

Under the catalytic action of Ag^+ diazoketones rearrange to ketenes which are converted into acids in aqueous solution:

$$CH_3-\overset{\overset{O}{\|}}{C}-CH=\overset{+}{N}=\overset{-}{N} \rightarrow CH_3-\overset{\overset{O}{\|}}{C}-\overset{\diagup}{\underset{\diagdown}{CH}} + N_2$$

$$CH_3-\overset{\overset{O}{\|}}{C}-\overset{\diagup}{\underset{\diagdown}{CH}} \rightarrow O=C=CH-CH_3 \xrightarrow{H_2O} HO-\overset{\overset{O}{\|}}{C}-CH_2-CH_3$$

This method is extensively used for synthesis of a homologue of the parent acid (Wolff).

Even the synthesis of diazoketones demonstrates the facile replacement of the hydrogens of the methylene group of diazomethane. This is supported by the possibility of formation of metal derivatives of diazomethane:

$$CH_2=\overset{+}{N}=\overset{-}{N} + (C_6H_5)_3CNa \rightarrow NaCH=\overset{+}{N}=\overset{-}{N} + \underset{\text{Triphenyl-methane}}{(C_6H_5)_3CH}$$

An interesting reaction is the photochemical decomposition of diazomethane, which leads to a polymer $(CH_2)_n$ via the formation of carbene, CH_2 (see Volume III). The interaction of such a fragment of diazomethane (the methylene radical, also called carbene) with olefins gives three-membered rings:

$$CH_2=CH_2 + :CH_2 \rightarrow H_2C\underset{\diagdown\ \diagup}{-}CH_2$$
$$\qquad\qquad\qquad\qquad\qquad\quad CH_2$$

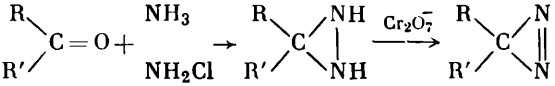
Diazomethane was originally believed to possess the three-membered ring structure

$$H_2C\underset{\diagdown}{\overset{\diagup}{N}}\!\!\|\,N$$

but this was disproved by electron diffraction studies of gaseous diazomethane, which showed the linear structure to be correct. Recently, Schmitz has accomplished the synthesis of cyclodiazomethane by oxidation of the corresponding hydrazine:

$$H_2C\underset{\diagdown}{\overset{\diagup}{NH}}\!\!|\,NH \xrightarrow{O} H_2C\underset{\diagdown}{\overset{\diagup}{N}}\!\!\|\,N + H_2O$$

This is a colourless substance, much less reactive than diazomethane. The route to cyclic diazomethane and its homologues, called **diazirines**, is as follows:



When heated diazirines partly lose nitrogen to form carbenes, RR'C, and partly isomerize into aliphatic diazo compounds.

VI. Principles of Quantum-Chemical Treatment of the Electronic Structure of Molecules*

(A) The Wave Function of the Ground State of Molecules

The theoretical foundation of modern concepts of the structure and interaction of atoms and molecules, in particular their electron shell structure and the nature of the chemical bond, is quantum mechanics. Atoms and molecules are typical examples of quantum-mechanical systems. The behaviour of a quantum-mechanical system is described by Schrödinger's equation and its states by solutions of this equation—so-called **wave functions.**

The wave function of the stationary state of a system depends on the space coordinates and on the spin-coordinates of all the particles of the system.** It is designated by the symbol

$$\psi(x_1, y_1, z_1, \sigma_1, \ldots, x_n, y_n, z_n, \sigma_n)$$

where n is the number of particles in the system; x_i, y_i, z_i ($i = 1, 2, \ldots, n$) are the space coordinates of the ith particle; σ_i is the spin-coordinate of the ith particle, which determines one of the two possible values of the projection of the intrinsic (i.e., spin) angular momentum of the ith particle on a certain specified direction.

The Pauli exclusion principle imposes the requirement of antisymmetry on the wave function of a system of electrons: when two electrons are exchanged, the wave function retains its absolute value but changes its sign.

A knowledge of the wave function of a quantum-mechanical system permits us to calculate the mean values of the various physical quantities for a state represented by a given wave function. The energy has an exact magnitude for the stationary state.

* This section was written by D. A. Bochvar.

** The *stationary state* is a state with a definite energy. We may, without loss of accuracy, disregard the time dependence of the stationary state in our treatment (see below).

A very important physical characteristic of a quantum-mechanical system is the square of the absolute value of the wave function* The product

$$|\psi(x_1, y_1, z_1, \sigma_1, \ldots, x_n, y_n, z_n, \sigma_n)|^2 d\tau_1, d\tau_2, \ldots, d\tau_n$$

where $d\tau_i = dx_i dy_i dz_i$ is, according to one of the principal postulates of quantum mechanics, the probability of a definite configuration of the system, at which for each value of i ($i = 1, 2, \ldots, n$) the ith particle is in the volume $dx_i dy_i dz_i$ containing a point (x_i, y_i, z_i) and has a spin-coordinate σ_i. According to this, the square of the absolute value of the wave function has evidently the sense of **probability density.**

For the formulation to be complete the expression "the probability of a definite configuration of the system" could be followed by "at a given time". But, as pointed out above, we digressed from the time dependence of the wave function of the stationary state, and this was permissible because, as can be shown, the square of the absolute magnitude of the wave function of the stationary state (or, what is the same thing, the distribution of probability for the stationary state) is independent of time.

Such a probability interpretation of $|\psi|^2$ implies that there is fulfilled the so-called normalization condition, i.e.,

$$\sum_{\sigma} \int |\psi|^2 d\tau = 1 \quad (d\tau = d\tau_1 \ldots d\tau_n)^{**}$$

The meaning of the normalization condition is very simple: at least one configuration of the system (in the sense indicated above) is reliably known to exist and the probability of a reliable event is 1.

Mathematical difficulties associated with the finding of exact wave functions for systems consisting of many particles, say, polyelectronic atoms and molecules, are so great that exact wave functions are known only for a few simple cases. Calculation of complicated systems is accomplished by means of various approximate methods of quantum mechanics. At present, quantum chemistry deals mainly with approximate quantum-mechanical calculations of the electron shells of atoms and molecules.

Most of the methods of quantum chemistry are based on the so-called orbital description in which the approximate wave function of an atom or molecule is built up, with account being taken of the

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* The numerical values of the wave function are, in general, complex numbers, but in many cases the wave function may be chosen real.

** The integral is taken over the entire $3n$-dimensional space in which $|\psi|^2$ is defined as a function of the $3n$ space coordinates, and the summation is taken over all the possible combinations of spin-coordinates of all the particles of the system (the number of such combinations is only 2^n).

Pauli principle, of one-electron wave functions, i.e., functions, each of which depends on the space coordinates of only one electron. Such single-electron wave functions are called **orbitals.** The orbitals of atoms are known as **atomic orbitals** (abbreviated to AO) and those of a molecule as **molecular orbitals** (MO).

Atomic orbitals are naturally also used as a "starting material" for building up the wave functions of molecules, which is in agreement with the usual concept of a molecule being a particle made up of atoms.

For the electron shell of an atom or molecule to be described in terms of orbitals the Pauli exclusion principle may be expressed thus: each orbital can accommodate only two electrons, and these two electrons must have opposite spins (in other words, they must have antiparallel spins).

It should be noted that the choice of orbitals in constructing one and the same wave function of a molecule as a whole is not, generally speaking, unique.

The antisymmetrical wave function of a molecule is normally sought for as a determinant or as a linear combination of determinants. The elements of such a determinant are so-called spin-orbitals. A **spin-orbital** is a one-electron wave function obtained from an orbital by multiplying it by the spin-function describing the spin state of a single electron. Since the spin angular momentum of the electron about a certain specified direction may have only two values $\left(+\frac{1}{2} \text{ and } -\frac{1}{2}\right)$, it follows that only two spin states of the electron are possible and, hence, two such spin-functions. They are usually designated by the symbols α for $\sigma = +\frac{1}{2}$ and β for $\sigma = -\frac{1}{2}$.

In most cases, the orbital methods of quantum chemistry are based on the so-called one-electron approximation in which each electron is regarded as being in a definite stationary state in the region of all the nuclei and the remaining electrons of the system (atom or molecule), the nuclei being usually assumed to be at rest.

Each approximate method of calculation, rather widely applicable in this field, gives rise to a specific theoretical language useful at a certain level of study and for a limited number of problems.

(B) The Electronic Structure of Atoms

In the one-electron approximation, the wave function of an atom is, as indicated above, made up of orbitals. To each orbital is assigned a definite set of characteristic **quantum numbers.** The set of quantum numbers of an atomic orbital includes the principal quantum number n, the orbital quantum number l and the magnetic quantum number m. The **principal quantum number** n may have the values

1, 2, 3, ... This quantum number defines the energy of the electron in a precise way for hydrogen-like atoms and only approximately for other atoms. In the latter case the energy depends, in addition, on the orbital quantum number l. The total number of electrons that occupy orbitals with the same value of n is often called a principal level (or shell).

The **orbital quantum number** l defines the orbital momentum of an electron. At a given value of n the orbital quantum number l may assume the values 0, 1, 2, . . ., $(n - 1)$. This number also defines the symmetry of the orbital. It thus also determines the symmetry

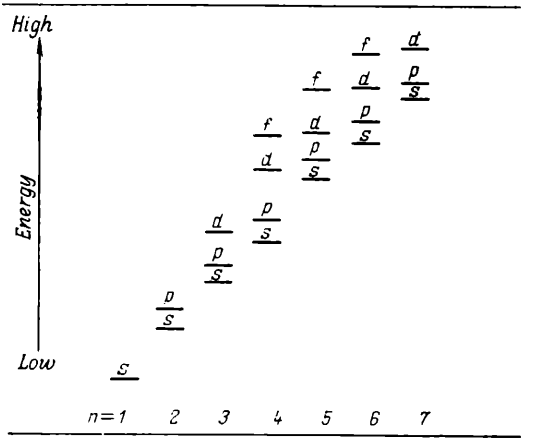

Fig. 2.5.
Orbital energy levels for neutral atoms.

of the distribution of the probability density and hence the symmetry of the spatial distribution of the charge on the electron (the so-called electron cloud of the orbital). The notation adopted for atomic orbitals, which is borrowed from atomic spectroscopy and classifies atomic orbitals according to the value of the orbital quantum number, is as follows: s $(l = 0)$, p $(l = 1)$, d $(l = 2)$, f $(l = 3)$, etc. The relation between the orbital quantum number and the electron energy can be seen from the energy-level diagram shown in Fig. 2.5.

The **magnetic quantum number** m defines the angular momentum of an electron about a specified direction. At a given value of l the quantum number m may take on the following $2l + 1$ values:

$$-l,\ -(l-1),\ \ldots,\ -1,\ 0,\ 1,\ \ldots,\ (l-1),\ l$$

The symmetry properties of atomic orbitals are of great importance for an understanding of the nature of the chemical bond. From the same point of view, the behaviour of the orbital with increasing distance from the atomic nucleus (the radial function of the orbital)

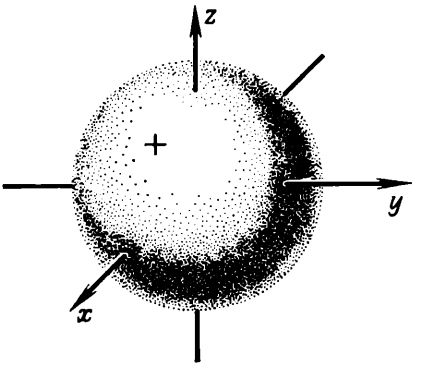

Fig. 2.6.
Boundary surface of a 1*s* orbital.

is essential. A graphical representation of the dependence of the atomic orbital on the space coordinates is impossible since it would require using a four-dimensional space. But we can make use of subsidiary techniques of planar representation providing a certain

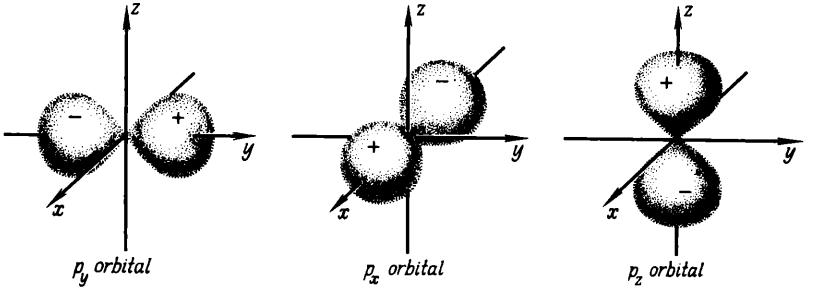

Fig. 2.7.
Boundary surfaces of 2*p* orbitals.

degree of vividness helpful in qualitative applications of the orbitals. Figures 2.6-2.8 show the so-called boundary surfaces for *s*, 2*p* and 3*d* orbitals.

This representation is qualitative in character and therefore the principal quantum number is immaterial in this case. The character of boundary surfaces in such a qualitative representation is largely

determined by the angular dependence and is therefore also valid for approximate atomic orbitals since the character of the angular dependence in this case is the same as for precise atomic orbitals.

The boundary surface delimits such a volume in a three-dimensional space that the probability of finding the electron within it is sufficiently high, and the value of the orbital on the surface itself is constant in absolute magnitude.* The subscripts signifying the

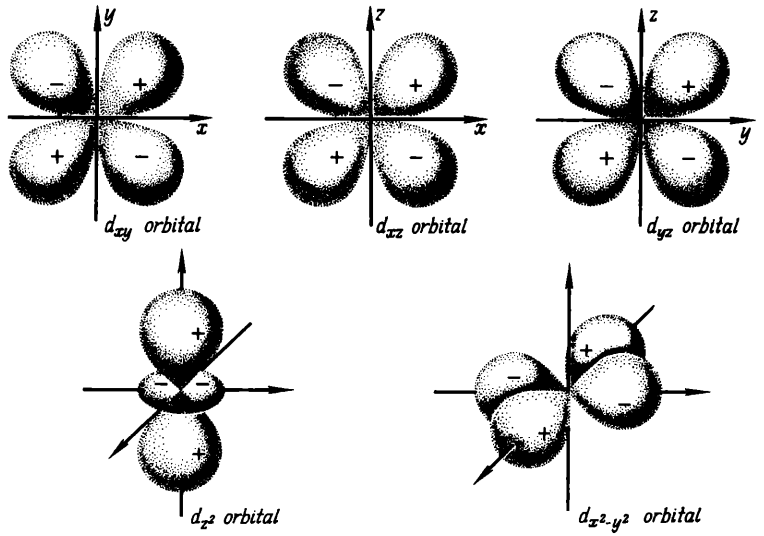

Fig. 2.8.
Boundary surfaces of 3*d* orbitals.

coordinates or the coordinate functions characterize the angular dependence of the atomic orbital. An atomic orbital with a given value of l is $(2l + 1)$-fold degenerate. This means that there are $(2l + 1)$ orbitals with the same value of energy; the *s* orbital is not degenerate, the *p* orbital is threefold degenerate, and the *d* orbital is fivefold degenerate (Fig. 2.8).

The *s* orbital has a spherical symmetry; the p_x, p_y and p_z orbitals have a definite clear-cut direction along the corresponding coordinate

* Hence, the value of $|\psi|^2$ (and of ψ^2 for a real orbital) on the boundary surface is also constant. Figures 2.6-2.8 give an impression of a three-dimensional space. But sometimes use is made of planar sections of boundary surfaces, and then the three-dimensional representation, of course, allows the character of change in the density distribution to be shown only in an approximate qualitative way. It must be borne in mind that the boundary surfaces shown in Figs. 2.7 and 2.8 do not pass through the coordinate origin.

axes and possess a cylindrical symmetry* relative to these axes. They are antisymmetrical relative to the coordinate planes yz, xz, xy** and, hence, these planes are respectively nodal for them (i.e., the p_x orbital turns to zero at all points in the yz plane; the p_y orbital does so at all points in the xz plane, and the p_z orbital turns to zero at all points in the xy plane). The symmetry of d orbitals is also shown in Fig. 2.8.***

The quantum numbers n, l, and m belong to orbitals and also to an electron in so far as the electron is contained in a particular orbital (occupies the given orbital). There is still another quantum number known as the **spin quantum number** s, which belongs more directly to the electron. This quantum number defines the orientation of the electron spin in a specified direction and has only two possible values: $+\frac{1}{2}$ or $-\frac{1}{2}$. Thus, the total set of quantum numbers for an electron in an atom consists of four quantum numbers: n, l, m, s. The electrons of an atom with the same values of n and l are called **equivalent electrons.**

For the electron shells of atoms depicted in monoelectronic terms the Pauli exclusion principle is often formulated more specifically: no two electrons in a given atom can have the same four quantum numbers n, l, m, and s.

The concept of electron spin and the Pauli principle describe the entire process of filling atomic orbitals with electrons in order of increasing energies, the number of electrons increasing with the positive charge of the nucleus. Therefore, from the viewpoint of the monoelectronic treatment, the sequence of the orbital energy levels,

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* The cylindrical symmetry of an orbital with respect to a given axis means that this axis is the rotation axis of the orbital, i.e., the function retains its value upon any rotation about this axis.

** That is, they change sign upon reflection in these planes but retain their absolute magnitude.

*** As regards the $2p$ and $3d$ orbitals shown in Figs. 2.7 and 2.8, it should be noted, for the sake of accuracy, that the p_z and d_{z^2} orbitals are accordingly identical with p_0 ($p_{m_l=0}$) and d_0 ($d_{m=0}$) (here m is the magnetic quantum number), which are real. The p_x and p_y orbitals are real linear combinations of complex p_{+1} and p_{-1} orbitals (where $+1$ and -1 are the values of m) and the d_{xy}, d_{xz}, d_{yz} and $d_{x^2-y^2}$ orbitals are various real linear combinations built up of d_{+1} and d_{-1} (d_{yz} and d_{xz}) and of d_{+2} and d_{-2}(d_{xy} and $d_{x^2-y^2}$). For example, the p_x and p_y orbitals are related to p_{+1} and p_{-1} as follows:

$$p_x = (p_{+1} + p_{-1})/\sqrt{2} \qquad \text{and} \qquad p_y = -i\,(p_{+1} - p_{-1})/\sqrt{2}$$

where i is the imaginary number.

The p_z and d_{z^2} orbitals have a cylindrical symmetry with respect to the z axis precisely because for them $m = 0$ (it is assumed that the z axis coincides with the physically defined direction). In the presence of a magnetic field, use should be made of orbitals with a definite value of the quantum number m, i.e., for example, not p_x and p_y but p_{-1} and p_{+1} orbitals, etc.

the spin and the Pauli principle determine the entire structure of the Mendeleyev system.

Certain characteristics of the shell and period in the Mendeleyev system are expressed quite simply as the functions of the quantum numbers n and l, respectively. It is the maximum possible number of electrons in each principal shell that is expressed by the principal quantum number of the shell, n:

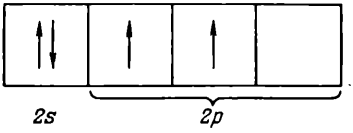
$$N_{max} = 2n^2$$

and the length of the period, L, is determined by the maximum value of the orbital quantum number l achieved actually in the period:

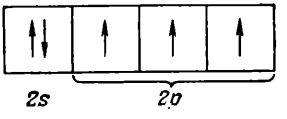
$$L = 2(l_{max} + 1)^2$$

The distribution of electrons in an atom in groups of equivalent electrons is called **the electronic configuration of the atom.** Thus, the electronic configuration of the carbon atom in the ground state is written as follows*: $1s^2 2s^2 2p^2$. In such a notation, however, the electrons of the closed subshells are usually omitted, so that in our example the electronic configuration of the carbon atom will be $2s^2 2p^2$.

It is often convenient to depict electronic configurations in more detail. For instance, for the ground state of the carbon atom we have



Here each arrow represents an electron and the directions correspond to two possible orientations of the electron spin. A positive spin $\left(s = +\frac{1}{2}\right)$ is indicated by an arrow pointing upward and a negative spin $\left(s = -\frac{1}{2}\right)$ by an arrow pointing downward. The electronic configuration of the ground state of the nitrogen atom is depicted by the following scheme:



In both cases, the number of electrons with parallel spins in the p orbitals (the number of p electrons for short) of the second shell is the maximum possible number for a given configuration. This is in

* The superscript 2 indicates the number of electrons in a given orbital.

accord with Hund's rule which states that for the ground state, within a group of equivalent electrons, the number of electrons with parallel spins is a maximum.*

(C) The Molecular-Orbital Method

The most widely used quantum-mechanical method of calculating the electron shells of molecules is at present the molecular orbital method (abbreviated to the MO method).**

The usual form of the molecular orbital method is an approximation called the linear combination of atomic orbitals (LCAO). In this approximation, molecular orbitals are considered to be linear combinations of atomic orbitals. The method is usually abbreviated LCAO-MO, which stands for a linear combination of atomic orbitals-molecular orbitals.

In this method, an assumption is made that the molecular orbital near each atomic nucleus differs rather little from the corresponding atomic orbital entering into the linear combination (more exactly, is proportional to it), which is in argeement with the chemical viewpoint that a molecule is made up of atoms, for which a part of the electrons, namely bonding electrons, have become common. Thus, in the LCAO-MO method it is assumed that each molecular orbital may be written in the following form:

$$\psi(\tau) = \sum_{i=1}^{n} c_i \varphi_i(\tau) \qquad (1)$$

where τ is the total number of space coordinates of the electron; φ_i ($i = 1, 2, \ldots, n$) are atomic orbitals (several atomic orbitals may belong to one and the same atom), and c_i are numerical coefficients. Further, for the sake of simplicity, it is assumed that φ_i and c_i are all real.***

According to what has been said earlier, the distribution of probability density and, hence, the distribution of the electronic charge

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* Hund's rule is generalized in an appropriate form to the electronic structure of the molecule too.

** The most general ideas of the MO method are also expressed in the Hartree-Fock self-consistent field (SCF) method. The various methods of calculation by the MO method and its theoretical language have been developed in the works of many investigators, primarily in those of Hund, Herzberg, Hückel, Mulliken, Coulson, Roothaan.

*** This assumption does not reduce the general character of the LCAO-MO method within the framework of our treatment.

density (electron density) in space for the molecular orbital $\psi(\tau)$ is expressed in the following form*:

$$\psi^2 = \sum_{i=1}^{n} c_i^2 \varphi_i^2 + \sum_{i,\, j(i \neq j)}^{n} c_i c_j \varphi_i \varphi_j \qquad (2)$$

The paired products $\varphi_i \varphi_j$ play an important role in the one-electron description of the electronic structure of atoms and molecules. These products multiplied by the volume element $d\tau$ and summed up

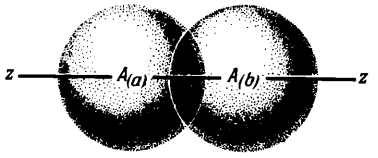

Fig. 2.9.

Overlap of two 2*s* orbitals in the molecule A_2; formation of a σ-bond.

(more exactly, integrated over the entire space) determine the so-called overlapping of the atomic orbitals φ_i and φ_j, which is a measure of coincidence.

The product $\varphi_i \varphi_j d\tau$ is often termed the **differential overlap** of the orbitals φ_i and φ_j.

The magnitude of the overlap of two atomic orbitals φ_A and φ_B of atoms A and B depends on a number of factors. In the first place, the overlap of φ_A and φ_B is different from zero only in those cases where these orbitals have the same symmetry relative to the *AB* axis, which connects the nuclei of atoms A and B. The overlap depends essentially on the types of symmetry of both orbitals by themselves. Account must also be taken of the dependence of the overlap of orbitals on the principal quantum numbers of both atomic orbitals. And, finally, the orbital overlap depends greatly on the distance between the nuclei of atoms A and B, so that even under the most favourable conditions indicated the overlap is close to zero if the A-B distance is sufficiently great.

Qualitatively, the effect of the symmetry of φ_A and φ_B relative to the $AB(z)$ axis on the orbital overlap is seen from a number of examples presented in Figs. 2.9-2.12.

In simplified versions of the MO method the interaction of the orbitals φ_A and φ_B is the stronger the greater is the amount of their overlap, and if the overlap is equal to zero, their interaction is then also equal to zero. Usually, in these forms of the MO method it is assumed that the interaction is proportional to the overlap.

* For brevity, the symbols for the coordinates are omitted in the orbital shorthand.

The normalization condition which forms the basis of the probability interpretation of the square of the absolute value of the wave function under the assumptions made above concerning φ_i and c_i is expressed for the molecular orbital $\psi(\tau)$ by the equation:

$$\int \psi^2 d\tau = \sum_{i=1}^{n} c_i^2 + \sum_{i,\, j(i \neq j)}^{n} c_i c_j s_{ij} = 1 \qquad (3)$$

where s_{ij} is the overlap of the atomic orbitals φ_i and φ_j (the overlap integral since s_{ij} signifies the integral $\int \varphi_i \varphi_j d\tau$; $0 \leqslant | s_{ij} | \leqslant 1$).

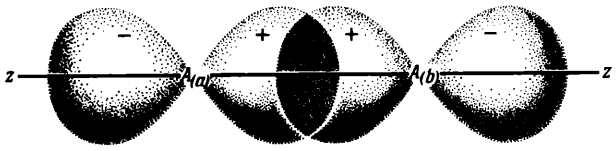

Fig. 2.10.

Overlap of two $2p_z$ orbitals in the molecule A_2; formation of a σ-bond.

In the simplest form of calculation based on the LCAO-MO method, which is the method meant further in the text, the integrals s_{ij} are neglected, and the normalization condition assumes the form:

$$\sum_{i=1}^{n} c_i^2 = 1 \qquad (4)$$

Then, on the basis of Eq. (4), each c_i^2 is interpreted as the probability of finding an electron near the ith atomic nucleus. The numerical values of the coefficients c_i are determined from the condition of the minimum energy of the electron in the $\psi(\tau)$ state.

If n atomic orbitals are chosen for calculation, then the LCAO-MO method provides, as a solution of the problem for the minimum energy of the electron in the $\psi(\tau)$ state, n molecular orbitals $\psi_i(\tau)$ with the corresponding values of the orbital energies ε_i. In this calculation, to one and the same value of orbital energy there may correspond more than one molecular orbital. If k molecular orbitals correspond to a certain value of ε_i, then this value of ε_i is said to be k-fold degenerate.

In the ground (lowest-energy) state of the molecule the electrons taken into account in calculation must naturally have the lowest values of orbital energy, i.e., they must fill orbitals with the lowest values of ε_i. Here the Pauli exclusion principle must be satisfied, and in the case of degenerate ε_i values the Hund rule must, generally speaking, be also obeyed. The sequence of the orbital energies arran-

ged in order of increasing values is called the energy-level diagram of the molecule (more exactly, the system of electrons considered in calculation). A reference point is chosen on the energy scale, which corresponds to the physical meaning of the problem (for example, the value of energy for a certain atomic orbital). Molecular orbitals whose values of orbital energy, ε_i, are below the reference point

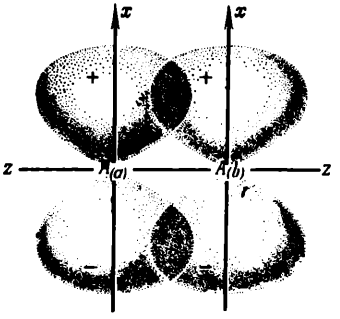

Fig. 2.11.
Overlap of $2p_x$ orbitals in the molecule A_2; formation of a π-bond.

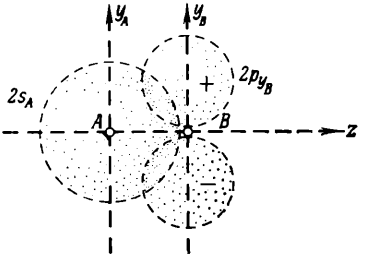

Fig. 2.12.
Overlap of angular factors of $2s_A$ and $2p_{yB}$ orbitals. With this orientation $2p_{yB}$ is equal to zero due to different symmetry of orbitals with respect to the AB (z) axis, and therefore the overlap of orbitals is also zero.

("zero" on the energy scale) are called **bonding orbitals**; orbitals with values of ε_i above the reference point are known as **antibonding orbitals**; and orbitals whose values of ε_i are equal to the reference point chosen on the energy scale are called **nonbonding orbitals.**

Bonding molecular orbitals have an increased electron density in the regions between the atomic nuclei, as compared with nonbonding and the more so with antibonding molecular orbitals.

In the simplest variants of the MO method the total energy of the system of electrons is equal to the sum of orbital energies ε_i multiplied by the corresponding "filling numbers" ν_i, i.e., the numbers of electrons filling the orbitals $\psi_i(\tau)$, and so

$$E = \sum_{i=1}^{n} \nu_i \varepsilon_i \qquad (\nu_i = 0,\ 1 \text{ or } 2)$$

In less simplified variants of the MO method, a correction is introduced into this equality.

The so-called **delocalization energy** (or the **conjugation energy**) is found by comparing the total π-electron energy of the molecule calculated by the MO method in the so-called π-electron approximation (see below) with the total π-electron energy calculated by the

same method for the same π-electron system but with no account taken of certain interactions between the atomic orbitals of contiguous atoms. The delocalization energy is defined as the difference

$$E_d^{\pi} = E_0^{\pi} - E^{\pi}$$

where E_0^{π} is the π-electron energy of the system which is regarded as the reference system; E^{π} is the π-electron energy of a given molecule.

For example, the π-electron energy of the benzene molecule is compared with the sum of the π-electron energies of three isolated π-bonds. The delocalization energy is also often termed the **resonance energy** in the Hückel π-electron approximation.

Since the molecular orbital method provides, in addition to filled orbitals, a certain reserve of vacant orbitals, it has at its disposal a natural and simple language for a physical description of the nature of the electronic spectrum of a molecule. The excitation of a molecule is defined here as the transition of electrons from filled orbitals to vacant ones.

The energy of the upper occupied (at least partly) molecular orbital, taken with an opposite sign, is termed the **ionization potential of the molecule** in the MO method, and the energy of the lowest vacant orbital, also taken with an opposite sign, is termed the **electron affinity of the molecule.**

The simplest forms of the MO method are parametric methods. This means that the calculation results are expressed in terms of certain main parameters. The values of these parameters are obtained by experiment, and in this sense the calculation is also semi-empirical. The main parameters in the calculation are usually so-called Coulomb integrals (α_i) which characterize the atomic orbital energies, and so-called resonance integrals (β_{ij}) which describe the interactions between atomic orbitals. In the language of the simplest forms of the MO method, the energies are often expressed in terms of β units, a certain resonance integral β being assumed as the unit of measurement.

An essential characteristic of molecular orbitals is their symmetry. The symmetry of molecular orbitals affects the strength of the chemical bonds formed by them.

In organic molecules, bicentric molecular orbitals are very common, for which the axis connecting the atomic nuclei is the rotation axis and which therefore have a cylindrical symmetry. This is an example of so-called σ-orbitals (sigma orbitals). Another very important and often encountered type of molecular orbitals is an orbital which is antisymmetric* with respect to the plane containing the

* The orbital is called *antisymmetrical* with respect to a certain plane if upon reflection in this plane it changes its sign, but retains its absolute value.

nuclear configuration of the molecule or a fragment of it. In chemistry, such orbitals are most frequently called π-orbitals, which however is not always consistent with a more rigorous classification in which the names and symbols of orbitals according to symmetry are introduced by the following definitions.

The molecular orbital $\psi(\tau)$ is defined as the σ-orbital if it has a symmetry axis, the rotation about which does not change the sign of $\psi(\tau)$. The σ-orbital always has a plane of symmetry.

The molecular orbital $\psi(\tau)$ is called a π-orbital if an axis can be specified for it, the rotation about which through 180° changes the sign of $\psi(\tau)$. The π-orbital has one and only one plane of antisymmetry passing through the axis indicated.

The molecular orbital $\psi(\tau)$ is termed a δ-orbital if an axis can be specified for it, the rotation about which through 90° changes the sign of $\psi(\tau)$. The δ-orbital has only two planes of antisymmetry passing through the specified axis.

More complicated types of orbital also exist. The role of the physically specified axes in this classification is played by the symmetry axes of molecules or their fragments.

In organic and organoelement chemistry, use is ordinarily made of a simplified classification of molecular orbitals which does not claim to be strict and complete. Namely, as has already been said above, σ-orbitals are orbitals with an axial symmetry, but sometimes the symmetry with respect to a certain plane is considered to be a characteristic feature of the sigma type of orbital; within the framework of the simplified classification, π-orbitals are known to be orbitals which are antisymmetrical with respect to the plane of the nuclear configuration of a molecule or a fragment of it.

From what has been said above it follows that the assignment of an orbital to this or that type of symmetry is always based on the choice of a certain element of symmetry (the axis of symmetry, the plane of symmetry, etc.) and also on the behaviour of the orbital with respect to the symmetry element chosen. It is therefore understandable that the assignment of orbitals to symmetry types in both classifications (i.e., in the more rigorous and in the simplified classification) may be different. Thus, the lowest-energy molecular orbital of the benzene molecule belongs to the sigma type in the more exacting classification, which in this particular case makes use, as a criterion, of the behaviour of the orbital with respect to the sixfold axis of the molecule, and to the pi type according to the simplified classification in which the criterion is the behaviour of the orbital with respect to the nuclear configuration of the molecule.

According to what has been said about the overlapping, the bond formed by a molecular orbital is the stronger the greater the amount of overlap of the atomic orbitals φ_A and φ_B of the neighbouring atoms. Since, in general, the overlap of atomic orbitals is greater

in the case of formation of a bonding σ-orbital than of a bonding π-orbital, it follows, as a rule, that σ-orbitals bind more firmly than π-orbitals.

In a qualitative treatment, the terminology and notation given above are also used for the bonds formed by molecular orbitals and one therefore speaks of σ-bonds, π-bonds, etc. For example, from what has been said about the relative stability of bonding provided by σ- and π-orbitals it may be concluded, in general, that σ-bonds are stronger than π-bonds.

The interpretation of the chemical bond concept in terms of molecular orbital theory is one of the main tasks in quantum chemistry,

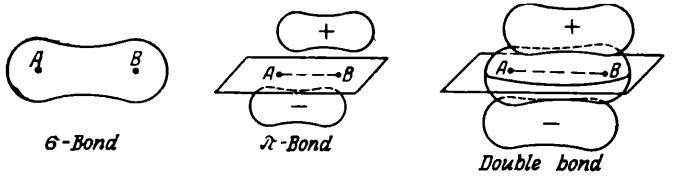

Fig. 2.13.

Representation of σ and π orbitals and a double bond with the aid of "boundary surfaces"

which has been satisfactorily solved in a qualitative way for a number of important cases. For instance, even an incomplete molecular-orbital description of diatomic molecules shows that atoms A and B can be bonded by more than one molecular orbital. Relatively simple is the molecular-orbital description of cases for which chemists have long used the concept of multiple (double, triple) bonds.

The σ- and π-orbitals and their combination, a double bond, are shown with the aid of boundary surfaces in Fig. 2.13.

As pointed out above, the numerical values of molecular-orbital coefficients are determined from the condition of the minimum energy of $\psi(\tau)$.

Each molecular orbital $\psi_j(\tau)$ can be represented as a set $\{c_{ij}\}$ of its coefficients, a certain arbitrary numbering being adopted for the atomic orbitals φ_i. The set $\{c_{ij}\}$ can be written in a more detailed form as $(c_{1j}, c_{2j}, \ldots, c_{nj})$*. With the aid of the $\{c_{ij}\}$ sets it is possible to determine a number of interesting and important characteristics of molecular orbitals and of the electron shells of molecules. For example, on the basis of the $\{c_{ij}\}$ sets one can determine, in a straightforward way, the concept of a k-centric molecular orbital, namely: if in the set $\{c_{ij}\}$ the k ($k \leqslant n$) coefficients are significantly

* That is, in the form of an n-dimensional vector, which reflects the algebraic character of the solution of the problem by the LCAO-MO method.

different from zero, and the remaining $(n - k)$ coefficients are negligibly small, the molecular orbital is called the **k-centric orbital.**

If $k = n$, then the molecular orbital may be regarded as **completely delocalized.** If $k < n$, and the coefficients $c_{i(1)j}$, $c_{i(2)j}$, . . ., $c_{i(k)j}$ are essentially different from zero, then the orbital is **localized** on atoms that have the atomic orbitals $\varphi_{i(1)}$, $\varphi_{i(2)}$, . . ., $\varphi_{i(k)}$. The bicentric orbital is the simplest special case of the localized molecular orbital. Since, generally speaking, bonding orbitals have a greater electron density in the region between the nuclei than nonbonding and antibonding orbitals, the k-centric bonding orbital has a more uniform electron density distribution than the k-centric nonbonding or antibonding orbital.

Knowledge of the coefficients c_{ij} enables one to describe, in terms of molecular orbital theory, certain features of the electron density distribution in a molecule, which are useful for the explanation of molecular reactivity. To express this kind of information, contained in $\{c_{ij}\}$ sets, a system of electron indices is introduced for a molecule, which is determined with the aid of coefficients c_{ij}. This system of electron indices is often written in the form of a so-called **molecular-orbital diagram.**

The main idea of the system of electron indices and the molecular-orbital diagram is as follows. With "rigid" atomic orbitals φ_i being specified *a priori*, the "flexible" characteristic which must reflect, at least to a first approximation, the principal features of electron density distribution arising as a result of the formation of a molecule, are exactly the $\{c_{ij}\}$ sets of molecular-orbital coefficients.

The system of electron indices defined below is applicable, in such a simple form, predominantly to π-electron systems of molecules, i.e., systems of electrons which are in the π-orbitals of the molecules. π-Electron systems are contained in molecules with multiple and conjugated bonds and their molecular-orbital calculations constitute the subject matter of the so-called pi-electron approximation, the simplest form of which is usually known as the Hückel pi-electron approximation.

The neglect of overlap integrals in the pi-electron approximation is a much more justified simplification than in calculations involving σ-orbitals since, in general, the overlap of atomic orbitals in molecular pi-orbitals is considerably less than in sigma orbitals.

Let a calculation by means of the LCAO-MO method for a problem concerning N electrons for n initial atomic orbitals φ_i lead to a set of n molecular orbitals ψ_j; let then the filling number of ψ_j (i.e., the number of electrons filling the orbital ψ_j) be equal to ν_j (the possible values of ν_j are 0, 1, 2) so that

$$\sum_{i=1}^{n} \nu_j = N$$

and the number of atoms be n. The first electron index is the **effective charge** on the ith atom and is introduced as follows. Let us determine

$$q_i = \sum_{j=1}^{n} \nu_j c_{ij}^2$$

It has been said above that c_{ij}^2 can be interpreted approximately as the probability of an electron in the state ψ_j to be found near the ith atomic nucleus; therefore the sum c_{ij}^2 extended to all n molecular orbitals ψ_i with account taken of the filling numbers, can be defined as the "effective number of electrons" on the ith atom. Now, by definition, the effective charge of the ith atom, Q_i, is the difference

$$Q_i = q_i^0 - q_i$$

where q_i^0 is the initial number of electrons supplied by the ith atom and taken into account in the calculation. It is obvious that Q_i may be positive, negative or equal to zero.

The second electron index is intended for the characterization of bonds formed by molecular orbitals. It is called the **bond order** and is introduced in the following manner.

We choose a pair of neighbouring atoms, say, with numbers r and s. Let j be the number of one of n molecular orbitals found in the calculation, i.e., let

$$\psi_j = \sum_{i=1}^{n} c_{ij}\varphi_i$$

so that the density ψ_j^2 is given by

$$\psi_i^2 = \sum_{j=1}^{n} c_{ij}^2\varphi_i^2 + \sum_{i,\,k=1;\ i\neq k}^{n} c_{ij}c_{kj}\varphi_i\varphi_k$$

From each molecular orbital ψ_j ($j = 1, 2, \ldots, n$) we take the product $c_{rj}c_{sj}$ at fixed r and s; from these products we set up a sum extended over all the ψ_j. Now we determine the bond order P_{rs} between the rth and sth atoms:

$$P_{rs} = \sum_{j=1}^{n} \nu_j c_{rj}c_{sj}$$

where ν_j are, as before, the respective filling numbers of molecular orbitals.

In the simplest variant of the LCAO-MO method, the bond order concept is usually applied only to a pair of neighbouring atoms. The bond order concept was introduced by Coulson. It is a generalization and more accurate definition of the concept of bond multiplicity from the viewpoint of molecular orbital theory and, generally

speaking, P_{rs} is not necessarily an integer.* Being a measure of the association between two neighbouring atoms, the bond order also characterizes the bond strength.

The two factors introduced—the effective charge and bond order—are generalized without difficulty to a case where the number of atomic orbitals is greater than the number of atoms. Indeed, in the above treatment the number of the atomic orbital is also simultaneously the number of the atom; if the number of orbitals is larger than the number of atoms, a summation must be introduced over the numbers of the atomic orbitals of one and the same atom (when the effective charge of the atom is to be determined) and also over all the pairs of atomic orbitals of the two neighbouring atoms chosen, which are included in molecular orbitals when the bond order is being determined.

A third electron index is the **free-valence number** (F) of an atom in a molecule. It is defined as follows.

Suppose that for the rth atom of a molecule we know the maximum possible value of the sum of bond orders in the molecule and let it be the constant $P_{\max}$. Now let $\sum_s P_{rs}$ be a sum of the orders of all the bonds in which the rth atom participates in the given molecule; here the summation index s covers the numbers of all the atoms adjacent to the rth atom. Then the free-valence number of the rth atom in the given molecule is determined thus:

$$F_r = P^{**}_{\max} - \sum_s P_{rs}$$

In the language of the pi-electron approximation the electron indices defined above are called **pi-electronic.** The pi-electronic bond orders are sometimes called the **mobile bond orders.** Within the framework of the pi-electron approximation, apart from the mobile bond orders, one often speaks of the full bond orders too, assuming that the order of each σ-bond is equal to unity by definition.

The system of electron indices for an organic molecule can be written on a diagram of its "σ skeleton"; the representation of the molecule obtained is called a **molecular diagram.**

Below is given the molecular diagram of 1,3-butadiene.

In the molecule of 1,3-butadiene, there takes place the sp^2 hybridization of the carbon (see page 325), and its σ skeleton is coplanar. The molecular orbital calculation of the butadiene molecule in the Hückel pi-electron approximation leads to the following molecular diagram (the C—C σ-bond orders are assumed to be equal to unity,

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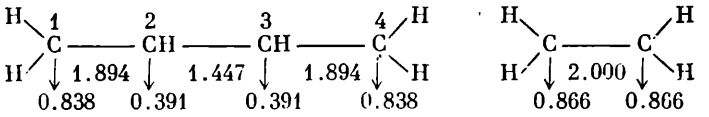
* P_{rs} may sometimes be negative too.

** For the carbon atom in an sp^2-hybridized state $P_{\max}$ has a value of 4.732 if it is assumed that the order of each σ-bond of the atom is unity.

the effective charges are equal to zero, the π-bonds are not shown; the molecular diagram of ethylene is given for comparison):

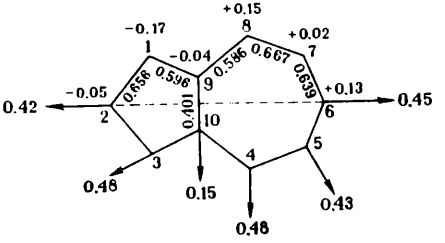


From the molecular diagram it is seen that the bonds between atoms 1 and 2 and between atoms 3 and 4 are almost double (the bond order is 1.894), the free-valence numbers F_1 and F_4 are close to the values of F in the ethylene molecule, and F_2 and F_3 are very close to the values of F in the benzene molecule (0.40).

The delocalization energy, as compared with the two localized π-bonds in terms of β units is equal to 0.47 (ca. 8 kcal/mole).

We shall also give the molecular diagram of azulene (an aromatic hydrocarbon which will be considered in a section devoted to non-benzenoid aromatic systems; see Volume IV).

The numbers placed at the upper corners of the rings designate the effective charges on the atoms; the arrows pointing from the corners are the free-valence numbers; the numbers along the lines of σ-bonds are the mobile bond orders; those symmetric with respect to the dash line are also the free-valence numbers.



In contrast to butadiene and benzene, the charges on the carbon atoms in azulene are different from zero.

The presence of a plane of symmetry enables one to specify each type of index only for half of the diagram. The apexes are numbered as usual.

On the basis of the molecular diagram of azulene, one can expect, for example, that electrophilic reagents will attack the molecule predominantly at the 1 position, nucleophilic reagents, predominantly at the 4 and 6 positions, and free radicals, at the 3 and 4 positions (if the ground state of the molecule is considered).

It should be noted that, apart from the electron indices introduced above, other interesting characteristics are also introduced on their basis, say, the various types of polarizability of atoms and bonds.

Finally, it should be noted that the electron indices and molecular diagrams have assumed great importance and at present a number of handbooks have been published on the subject (the handbooks written by Coulson and Streitwieser, by Streitwieser and Brauman, by Heilbronner).

Whereas the main idea of the LCAO-MO method is the transition from the atomic orbitals of isolated atoms to the molecular orbitals of molecules in accordance with the symmetry of problems and the Pauli principle, another approach is also possible.

Let us imagine that the nuclei of atoms have coalesced into a single, more complicated nucleus and that the electrons have been distributed among the atomic orbitals of the resultant "combined atom" according to the sequence of the energy levels in it and the Pauli principle. Then a question may arise as to what molecular orbitals will be built from the atomic orbitals of the combined atom and will be found to be filled up at a certain separation of the nucleus of the combined atom into the original atomic nuclei (again in accordance with the symmetry and the Pauli principle). This variant of the MO method is called the **combined-atom method.**

(D) Structure Resonance or Mesomerism

The second widely employed method of describing certain features of the electronic structure of molecules is associated with another method of calculation of the electron shells of molecules—the so-called **valence bond (VB) or resonance method.** As compared with the molecular orbital description, this method is much more qualitative in character. On the other hand, the principal ideas of valence bond theory are widely applicable because of its intimate connection with the apparatus of chemical structural formulas.

The valence bond theory was worked out a little earlier than the molecular orbital method. It originated as a generalization of the method used in 1927 by Heitler and London for calculating the hydrogen molecule. This calculation was used to qualitatively elucidate the quantum-mechanical meaning of the valence line which is the principal symbol in the language of chemical structural formulas. From the calculation of the hydrogen molecule made by Heitler and London it follows that the valence line has the sense of a pair of electrons with antiparallel spins. The wave function of this electron pair provides, in the space between two atomic nuclei, a localization of the negative charge of the electrons sufficient for the two nuclei to be held at such a distance that one may regard the entire system formed by two atoms as a molecular entity.

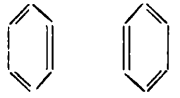
In the Heitler-London method, which was subsequently generalized in the works of Heitler, Rumer, Slater, Pauling and a number of

other investigators, approximate wave functions were a means of translating chemical structural formulas into the language of the approximate method of quantum-mechanical calculation.*

For molecules whose structures can be expressed rather unambiguously by means of a single structural formula (for example, methane, ethylene), it is not difficult to formulate an approximate wave function on the basis of atomic orbitals (directly or constructing first the approximate wave functions of individual atoms) in the VB method. There are, however, many molecules for which there is not such an unambiguity. Such are, for example, molecules with systems of conjugated bonds or molecules with internal ionization. Generally speaking, a sufficiently unambiguous representation with the aid of a single structural formula is possible only for molecules whose bonds may be considered bicentric to a satisfactory approximation.

The treatment, within the framework of valence bond theory, of molecules that cannot be represented unambiguously with the aid of the symbolism of structural formulas led to the formulation of the widely used and convenient (when the number of possible representations by means of structural formulas is not too great) idea of structure resonance.**

A classical example of a molecule that cannot be represented by a single structural formula is the benzene molecule. Even from symmetry considerations it is clear that formulas I and II (the so-called Kekulé structures)



I II

are quite equivalent forms and must equally depart from the actual picture in the benzene molecule which has a sixfold axis of symmetry. If, in accordance with the recipe of valence bond theory, we construct approximate wave functions corresponding to the structural formulas of benzene I and II, say, the functions ψ_I and ψ_{II}, then the same will be valid for them.

The idea of structure resonance consists in the following. The structure of a molecule, the representation of which by a structural

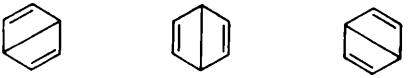
* The VB method, just as the MO method, is a version of the orbital description of the electronic structure of the molecule. Like the MO method, it may also contain the pi-electron approximation. The consistent and sufficiently complete developments of the VB and MO methods allow us to establish that both methods have, in principle, a common foundation as far as the form of the wave functions is concerned.

** The term *resonance* is associated with the formal analogy between the equations of quantum-mechanical calculations of the energy and the equations describing the phenomenon of resonance in the theory of oscillations.

formula is ambiguous, should be pictured by a set of probable structural formulas. This means that for the approximate quantum mechanical calculation of such a molecule it is necessary to build the best linear combination of regular symmetry from the wave functions corresponding to individual probable structural formulas.* For example, the following wave function should be constructed for the ground state of the benzene molecule:

$$\psi = c_{\mathrm{I}}\psi_{\mathrm{I}} + c_{\mathrm{II}}\psi_{\mathrm{II}}$$

In this particular case it would be easy to show that $c_{\mathrm{I}} = c_{\mathrm{II}}$. But if we treat the problem in a more detailed manner, we should also take into account the three equivalent Dewar structural formulas:



III IV V

Then one should build a linear combination of five respective wave functions:

$$\psi = a(\psi_{\mathrm{I}} + \psi_{\mathrm{II}}) + b(\psi_{\mathrm{III}} + \psi_{\mathrm{IV}} + \psi_{\mathrm{V}})$$

Since in this case the functions ψ_{I} and ψ_{II}, on the one hand, and the functions ψ_{III}, ψ_{IV}, and ψ_{V}, on the other, are not equivalent, it becomes necessary to find the best linear combination, i.e., the best values of the coefficients a and b. Such values of a and b are found from the condition of the minimum energy of the molecule. The wave function ψ is termed the resonance of structures ψ_{I}, ψ_{II}, ψ_{III}, etc., and ψ_{I}, ψ_{II}, ψ_{III}, etc., are called resonating structures.

It would be incorrect to think that the properties of the molecule, which are calculated with the aid of the function ψ, would be intermediate between the properties of the structures ψ_{I}, ψ_{II}, ψ_{III}, etc. The actual picture is best illustrated by the simplest case of only two resonating structures:

$$\psi = a\psi_{\mathrm{I}} + b\psi_2$$

Even for the multidimensional** density we have (assuming the

* Since, in general, there exist linear relations between the wave functions, it is common practice to choose the smallest (as to the number of functions) set of linearly independent functions, which is complete in the sense that all the other possible functions (missing in the set) are determinable through it. Such a set is often called a *set of canonical structures*.

** Since ψ is here a many-electron approximate wave function, then ψ^2, i.e., the corresponding density, is also determined in the multidimensional configurational space.

functions and coefficients to be real):

$$\psi^2 = a^2\psi_1^2 + b^2\psi_2^2 + 2ab\psi_1\psi_2$$

that is, there appears the "interference" term.

Analogous "interaction terms" also appear in the calculation of the mean values of the physical quantities by using the rules of quantum mechanics (since the values of the physical quantities depend on the wave function not linearly but in a quadratic manner). It is especially important that the value of the energy calculated for the wave function, which is a resonance hybrid of several structures, is lower than for each resonating structure separately. This is understandable because the hybrid of resonating structures is their linear combination which is the best in the sense that it corresponds to the minimum energy that can be obtained with the aid of linear combinations of the given resonating structures.

For the energy lower than that of any of the contributing structures to correspond to the resonance hybrid (for the molecule to be "stabilized"*), it is necessary that the structures satisfy the following conditions:

1. The geometry of the nuclear configurations of the structures must be identical or nearly identical.
2. The number of unpaired electrons for the structures is assumed to be the same.
3. The energies corresponding to individual structures (i.e., calculable with the aid of corresponding approximate functions built in accordance with the same rules of the VB method or estimable with the aid of certain additive schemes from experimental data), must not differ too strongly from one another.

The difference between the energy for the energetically most favourable structure and the energy for the resonance hybrid is often called the **resonance energy** of the molecule.**

In using the resonance method for describing the electronic structure of molecules, one should always remember that *individual resonating structures do not represent the physically real states of the molecule.*

In the language of structural formulas the structure resonance is expressed by a double-headed arrow placed between the two resona-

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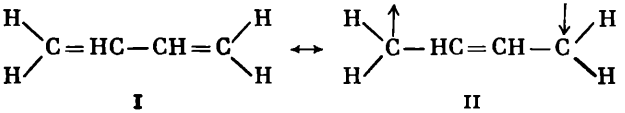
* In other words, the best linear combination of structures sought for should not reduce (or nearly reduce), in a trivial way, to the only energetically most favourable structure. Condition *2* is especially strict, then comes the less strict condition *1*; condition *3* is not too rigorous, but if it is not fulfilled, the stabilization may be reduced to a very low value.

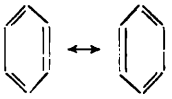
** It should be noted that in the pi-electron approximation of the MO method, the resonance energy may be likened to the concept of delocalization energy which is also sometimes referred to as the resonance energy.

ting forms of a molecule. For example, in the case of the butadiene molecule



I II

The resonance hybrid of two Kekulé structures for benzene is written as follows:



The butadiene molecule is described qualitatively in the language of the resonance theory as a resonance hybrid of the forms I and II, with a greater contribution from the structure I.

The *contribution to the resonance hybrid* is defined as the square of the absolute value of the coefficient with which the corresponding wave function is included in the linear combination representing the resonance hybrid. It should be noted that with this definition of the structure contribution the overlap of structures is neglected.

In conclusion, it is important to note that the specific feature of this approach to the description of the electronic structure of a molecule is not the formation of a linear combination of wave functions (which is a rather general method typical for quantum mechanics in general) but the choice of functions for building a linear combination. It is also essential here that the wave functions selected for this purpose are the approximate many-electron wave functions of the molecule as a whole.

(E) Hybridization of Atomic Orbitals and the Valence State

All the physical and chemical properties of the methane molecule, which have been studied experimentally, lend support to the equivalence of the four hydrogen atoms attached identically to the carbon atom in the molecule having the symmetry of a regular tetrahedron. As far back as 1879 van't Hoff and LeBel came to the conclusion that the methane molecule has four equivalent bonds between the carbon atom and the four hydrogen atoms which occupy the apexes of a regular tetrahedron and are at the same distance from the carbon atom.

The molecular-orbital calculation of the methane molecule with account taken of all the electrons on the carbon atom and the four electrons of the hydrogen atoms leads to the following picture of the

electron shell of the molecule: five bonding molecular orbitals are filled with ten electrons; the lowest-lying (lowest-energy) orbital is almost identical to the atomic 1*s* orbital of the carbon atom and has basically no relation to the chemical bond between atoms; of the remaining four bonding molecular orbitals the one, more symmetric, corresponds to the lower energy than the other three, which are less symmetric and belong to the same, triply degenerate value of energy; besides, the calculation provides four vacant antibonding orbitals.

Individual chemical bonds and molecular orbitals are not observable objects but are only theoretical structures, which belong to the various levels of consideration. A question arises: Is there a general theoretical foundation on the basis of which it would be possible to establish a correspondence between the picture of a system of four equivalent bonds and that of four bonding molecular orbitals one of which differs from the other three in symmetry and energy.

The situation described is quite typical. Therefore the solution of the problem is in fact very general in character. The trend in which the solution should be sought for is suggested by the following considerations: to solve problems that have an exact physical significance, one must, strictly speaking, make use of the wave function of the entire molecule, while the molecular orbitals themselves are basically a specific means of constructing the wave function of the molecule in the MO method.

The wave function of the molecule, which is built up of the molecular orbitals mentioned above, leads to a regular symmetry in the electron density distribution and is not in conflict with experimental data. As regards the molecular orbitals, they have been determined not quite unambiguously.

The approximate wave function of a molecule is built up of molecular orbitals in such a manner (determinant or a linear combination of determinants) that certain transformations can be performed simultaneously over all the molecular orbitals involved; the wave function itself is invariant to (i.e., remains unchanged by) these transformations. It turns out that the wave function of the methane molecule can be expressed in terms of new orbitals, four of which can, to a sufficient degree of approximation, be considered bicentric and localized along the four lines connecting the atomic nucleus of the carbon atom with the nuclei of the hydrogen atoms.

The lowest-lying orbital retains its character of the atomic 1*s* orbital of carbon and four new orbitals are sigma orbitals and are called **equivalent** orbitals in the sense that they can be converted to one another as a result of rotations and reflections which re-build the regular tetrahedron. They are therefore equivalent in the same sense in which the four C—H bonds are equivalent. The same applies to molecules containing only single bonds and isolated multiple bonds.

In the case of molecules with conjugated bonds the reduction to bicentric orbitals is impossible, and as a result of analogous transformations the delocalization of molecular orbitals is not removed in a sufficient degree; this reflects somewhat the conception of the resonance hybrid in the MO method.

The equivalent orbitals found in this way are sometimes called **bond orbitals.**

Localized equivalent orbitals may be regarded as linear combinations of atomic orbitals which are understood in a new, broader sense. Let us return to the methane molecule. The four equivalent orbitals may be represented as linear combinations built of the atomic 1*s* orbitals of the hydrogen atoms and the atomic orbitals of the carbon atom of the type

$$\frac{1}{2}[(2s)+c_1\,(2p_x)+c_2\,(2p_y)+c_3\,(2p_z)]$$

where the symbols (2*s*) and (2*p*) designate the atomic *s* and *p* orbitals of the carbon atom with the principal quantum number of 2, and c_i ($i = 1, 2, 3$) $= \pm 1$*. Atomic orbitals which are linear combinations of the atomic orbitals of one and the same atom are called hybridized orbitals, and their formation is known as the hybridization of atomic orbitals. The concept of hybridized atomic orbitals had been developed before the above theoretical situation was discovered, which accounts for the relation between delocalized molecular orbitals and equivalent localized orbitals. When working out qualitatively the system of quantum-chemical foundations of stereochemistry, Pauling and Slater, independently of each other, introduced in the period 1928-1931 the concept of hybridization which was successfully used in subsequent years for solving concrete chemical problems.

The concept of hybridization is the basis of the theory of directed valency. This theory originated and developed independently of the molecular orbital method**, mainly in connection with the calcula-

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* The four sets of c_i are: (1, 1, 1), (1, —1,—1), (—1, 1, —1), and (—1, —1, 1).

** The concept of the hybridization of atomic orbitals was derived earlier in the text from a special, though very important, case of the molecular orbital. Such a procedure, however, must not imply that the hybridization concept is important to the MO method. Though in a number of cases in the MO method, namely in the utilization of equivalent orbitals, the form of the molecular orbitals calculated allows us to introduce here the hybridization of atomic orbitals, nevertheless the general idea of the hybridized state of the atom has lost its significance in the MO method. Because of the more general approach in the MO method the simple rules, which are obeyed by the hybridization concept within the framework of directed valency theory, cease to be sufficiently general in the MO method.

tion apparatus in the original forms of valence bond theory. It has gained wide acceptance in a qualitative form too.

Let us consider some of the most important examples of application of the hybridization concept.

The hybridization of the atomic orbitals of the carbon atom described above is not the only one. Since, apart from the atomic 2*s* orbital, it also involves all the three 2*p* orbitals of carbon, this type of hybridization is designated by the symbol sp^3 (Fig. 2.14).

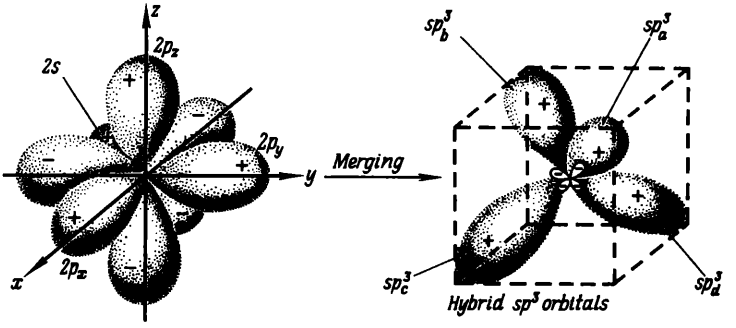


Fig. 2.14.
Formation of four sp^3 hybrid orbitals (tetrahedral hybridization).

Apart from the sp^3 hybridization, two other types of hybridization are also important for the carbon atom, namely, those designated by the symbols sp^2 and *sp*. Thus, in sp^2 hybridization the linear combination includes two 2*p* orbitals in addition to the atomic 2*s* orbital, and the third *p* orbital is retained as such (Fig. 2.15).

The *sp* hybridization leads to the formation of a linear combination of an atomic 2*s* orbital with one atomic 2*p* orbital of the carbon, and two *p* orbitals remain unchanged (Fig. 2.16).

Whereas the atomic *s* orbital has no directional character, the *p* orbital is directed along a definite axis but is distributed uniformly along this axis (in both directions from the coordinate origin connected with the atomic nucleus). The sign is immaterial in this respect.

All the three types of hybridized orbital are oriented almost completely in one direction from the coordinate origin and are therefore especially suitable for being overlapped by the atomic orbitals of other atoms of similar symmetry.

As pointed out above, in sp^3 hybridization, four hybridized orbitals are oriented away from the nucleus of the carbon atom to the apexes of a tetrahedron, which may be somewhat irregular in the presence of different substituents.

In the sp^2 hybridization, the axes of three hybridized orbitals lie in a single plane and are oriented towards the apexes of a regular triangle (the symmetry is trigonal). The pure p orbital is directed perpendicular to the plane of hybridized orbitals.

In sp hybridization both hybridized orbitals have a common axis of cylindrical symmetry but are oriented in different directions from the origin (i.e., from the nucleus of the carbon atom). Two pure p orbitals have mutually perpendicular axes and mutually perpendicular nodal planes intersecting along the symmetry axis of the hybridized orbital.

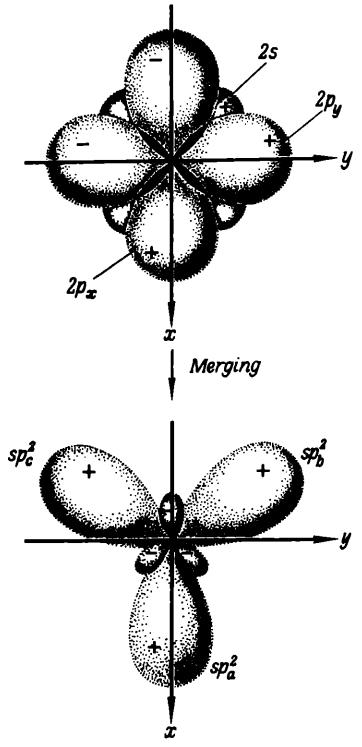


Fig. 2.15.
Formation of three sp^2 hybrid orbitals (trigonal hybridization).

The sp^3 hybridization is typical of the carbon atom in saturated compounds; sp^2 hybridization is characteristic of compounds with double bonds at the carbon atom (isolated or conjugated); compounds with triple bonds at the carbon atom and with cumulative double bonds show sp hybridization.

The hybridization concept is closely associated with the concept of the valence state of the atom. The meaning of the valence state may be illustrated by a typical example. Let us perform a thought experiment (which is absolutely infeasible) with the methane molecule. Suppose that the distances between the atomic nuclei in the methane molecule increase infinitely in a certain way but the electron shell of the molecule* undergoes a change during which the principal qualitative features of its geometry are retained. The electrons are allowed "to forget their host", but in each bond the electrons are equally distributed among the atomic nuclei. When the nuclei are sufficiently remote from one another, the carbon atom is found to be "carefully withdrawn" from the molecule, the equivalence of the

* In our treatment, the 1s orbital of the carbon atom is not included in the electron shell of the molecule.

four hybridized atomic orbitals directed tetrahedrally being retained. The resultant fictitious state is known as the valence sp^3 state. None of the states that may be actually observed in reality by spectroscopic methods corresponds to this state.* If we wanted to calculate its energy (which can be done in a formal way), we would find that

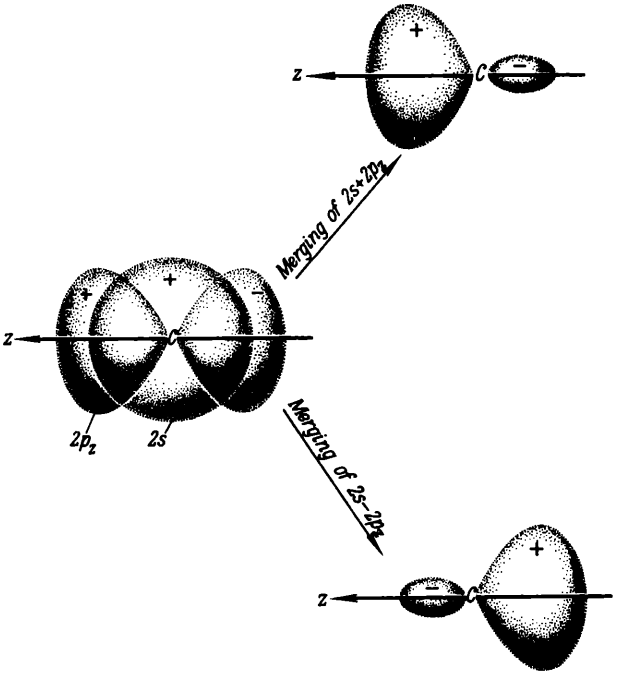


Fig. 2.16.
Formation of two *sp* hybrid orbitals (diagonal hybridization).

it is much higher than the energy of the ground state with the configuration $1s^22s^22p^2$ and exceeds somewhat the energy of the excited state with the configuration $1s^22s^12p^3$ arising upon transition of one electron from the $2s$ orbital to the $2p$ orbital which is vacant in the ground state. Figure 2.17 also shows schematically the purely qualitative relation between the energies indicated.

The bond formation energy compensates, with excess energy ε, for the loss of the energy spent for the excitation of the "valence

* From the quantum-mechanical standpoint, the valence state is a "blend" of some spectroscopically observable "pure" states (in the statistical sense rather than in the sense of their linear combination).

state" due to the increased overlap of the hybridized atomic orbitals of the carbon atom with the atomic 1*s* orbitals of the hydrogen atoms.

In reality, the process of formation of the methane molecule does not proceed through the stage of the "valence state" of the isolated atom. When the atoms approach each other, they begin to unite

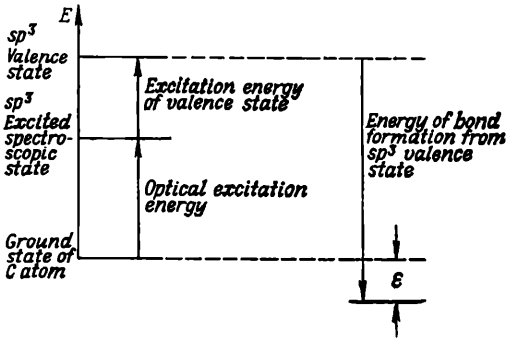


Fig. 2.17.

Diagram (qualitative) of the ratio of the energies of the carbon atom in the ground state, sp^3 excited state and sp^3 "valence state".

into a molecule, though loose at first, this process being accompanied by a gradual change in the nature of the orbitals.

Note that in the case of the tetravalent carbon atom the sp^3-hybridized valence state is sometimes called the **first valence state**, the sp^2-hybridized state—the **second valence state** and the *sp*-hybridized state—the **third valence state.**

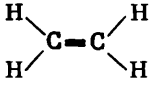
Hybridization and the valence state are supplementary theoretical conceptions. Neither hybridized atomic orbitals nor the valence state of the atom are as such a spectroscopically proved fact.

Chapter 3

Unsaturated Compounds

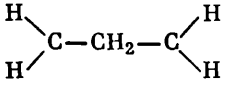
3.1. Olefins (Alkenes)

The homologous series of **olefins** or **alkenes** (according to the Geneva nomenclature) begins with ethylene

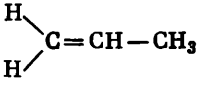


It is this circumstance and also the fact that methylene, which should have been the first homologue in this series, does not exist in the stable state, were the decisive factors in adopting the concept of the double bond as a characteristic structural feature of unsaturated hydrocarbons.

The second decisive argument in favour of the presence of a double bond in olefins was that the unsaturated carbon atoms in them are always found to be in pairs and are neighbours. For example, no unsaturated compounds of the type



exist but there are compounds such as

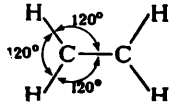


that is, unsaturated carbon atoms cannot be trivalent.

As has already been pointed out, the unsaturated carbon atoms in olefins and in their derivatives are in the second valence state. In distinction to the first valence state, which is characteristic of saturated compounds (the "tetrahedral" carbon with four equivalent valences directed at an angle of 109°28′ to one another—the sp^3

hybridization of electron orbitals), the carbon atom in the second valence state has only one *s*- and two *p*-orbitals hybridized (sp^2 hybridization), these forming three identical orbitals. The corresponding σ-bonds (single bonds) are oriented at an angle of 120° to one another and lie in the same plane. The third *p*-orbital of the carbon atom is not hybridized.

In olefins, such carbon atoms are linked in pairs. In ethylene, for instance, they form a planar figure of the type



The two *p*-orbitals (one at each carbon atom), which do not take part in the formation of the five σ-bonds in the ethylene molecule would occupy a space at the non-linked carbons, approximately restricted by a "spatial octet" (the figure of rotation of the eight about the longitudinal axis)* with a long axis perpendicular to the plane of three σ-bonds and a centre coinciding with the centre of each carbon atom. In carbon atoms which are joined to each other by a single bond (a σ-bond), these spatial octets merge into an orbital common to both *p*-electrons, which is accompanied by the liberation of energy (about 64 kcal/mole). These electrons form a so-called π-bond, that is, a second bond in the double bond. A π-bond is considerably less stable energetically than the sigma bond in C=C (83 kcal/mole) and is much more readily polarizable.

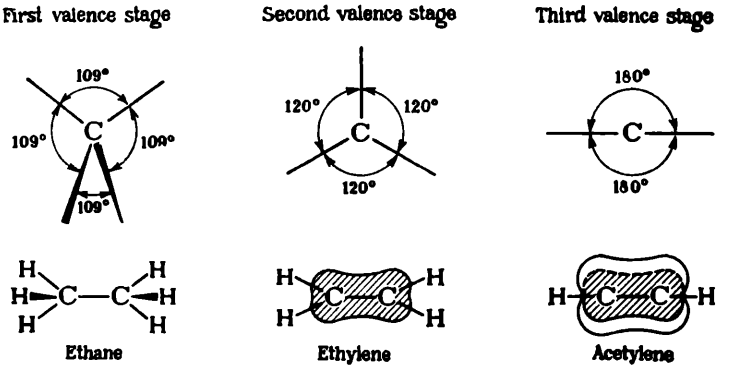
The presence of a double bond in a molecule manifests itself mainly in the fact that the sigma bond can no longer rotate about the axis, which is characteristic of saturated compounds, and the configuration of an olefin becomes stably planar, which gives rise, as a consequence, to geometrical isomerism (this phenomenon was mentioned on page 273 and will be considered in detail below).

The presence of a π-bond is characteristic not only of olefinic compounds. In the carbonyl group C=O the oxygen and carbon are linked together also by a π-bond. In nitriles, R—C≡N, the carbon and nitrogen are attached to each other by one σ-bond and two π-bonds. The same character is shown by the bonds in acetylenes, R—C≡C—R, which will be discussed later.

If carbon atoms are joined by two π-bonds with 4 *p*-electrons, then for the remaining three σ-bonds —C—C— there will be hybridized, for each carbon atom, one *s*- and one *p*-orbital (*sp* hybridization). This is the third valence state of the carbon atom in which both σ-bonds lie on a single line, and the orbitals of two π-bonds formed

* For the exact meaning of steric hindrance, see p. 307.

by *p*-electrons occupy in space the site of four paired, mutually perpendicular and intermingled spatial octets.

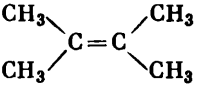


There is no geometrical isomerism in acetylenes.

The specific properties of the π-bonds in olefins and the manifestation of their unsaturated character will be clear from the description of the properties of olefins.

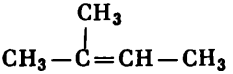
A. Nomenclature

The trivial names of olefins or alkenes are built by adding the ending *-ene* to the name of the corresponding radical of a saturated hydrocarbon (ethylene, propylene, butylenes, *n*-amylene, isoamylene, hexylenes, etc.) or they take their name from ethylene, the simplest member of the series; for example,


Tetramethylethylene

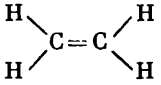
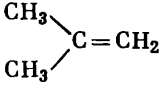
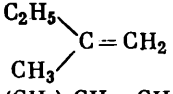
And, finally, according to the IUPAC system, an alkene is given the systematic name of the corresponding alkane with the final *-ane* changed to *-ene*: ethene, propene, butene, etc.

In this case, the name of an alkene is preceded by a numeral—the number of the carbon atom from which the double bond originates. For example,


2-Methyl-2-butene

Sometimes the position of the double bond is designated by the Greek letter Δ with the number of the atom as an exponent: Δ^2-methylbutene.

TABLE 3.1. Alkenes or Olefins

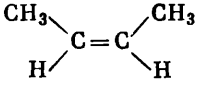
Formula	Name			m.p., °C	b p., °C	Density d_4^{20}
	trivial	IUPAC or GENEVA	ethylenic system			
	Ethylene	Ethene	Ethylene	−169.4	−103.9	0.596 (d_4^{-102})
$CH_3-CH=CH_2$	Propylene	Propene	Methylethylene	−185.2	−47.0	0.609 (d_4^{-47})
$CH_3-CH_2-CH=CH_2$	α-Butylene	1-Butene	Ethylethylene	−130.0	−5.0	0.668 (d_4^0)
$CH_3-CH=CH-CH_3$	Pseudobutylene	2-Butene	1,2-Dimethyl-ethylene			
	cis-			−139	+3.7	
	trans-			−105	+1	0.635
	Isobutylene or γ-butylene	2-Methylpropene	1,1-Dimethyl-ethylene	−140.3	−6.9	0.5942
$CH_3-CH_2-CH_2-CH=CH_2$	α-Amylene	1-Pentene	*n*-Propylethylene	−138.0	29.9	0.6405
$CH_3-CH_2-CH=CH-CH_3$	β-Amylene	2-Pentene	Methylethyl-ethylene	−139	36.9	0.6515
	γ-Amylene	2-Methyl-1-butene	1-Methyl-1-ethyl-ethylene	−137.6	31.2	0.650
$(CH_3)_2CH-CH=CH_2$	α-Isoamylene	3-Methyl-1-butene	Isopropylethy-lene	−135	25.0	0.648
$(CH_3)_2C=CH-CH_3$	β-Isoamylene	2-Methyl-2-butene	Trimethylethy-lene	−124	38.4	0.668 (d_4^{13})

In the chemistry of the derivatives of olefins, just as in the case of the derivatives of alkanes, use is often made of the "radical" nomenclature (recall, for example, such names as ethyl chloride). Radicals that contain a double bond are given the following names: **vinyl** or **ethenyl**, $CH_2=CH-$; **vinylidene**, $CH_2=C<$; **allyl**, $CH_2=CH-CH_2-$; **propenyl**, $CH_3-CH=CH-$.

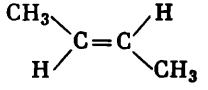
The names and physical properties of olefins are given in Table 3.1.

VII. Geometrical Isomerism I

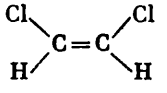
The rotation of groups of atoms about a carbon-carbon σ-bond requires only such an amount of energy (2-5 kcal/mole) which is easily supplied from the surrounding medium even at room or lower temperatures. It is this rotation which is responsible for the absence of **rotational isomers (conformers)** as individual chemical entities. The situation is different with the rotation about the double bond, in which case the rupture of the π-bond is needed, and hence about 60 kcal/mole must be consumed for the C=C grouping. Therefore there are isomers of all olefins or their derivatives with no plane of symmetry passing through the two carbon atoms joined by a π-bond perpendicular to the plane of the molecule. This spatial isomerism—**stereoisomerism**—is called in this case **geometrical isomerism.** The following are examples of geometrical isomers:



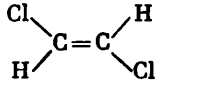
cis-2-Butene (m.p. −139°C; b.p. +3.7°C)



trans-2-Butene (m.p. −105°C; b.p. +1°C)



cis-Dichloroethene (b.p. +60°C; dipole moment 1.89D)



trans-Dichloroethene (b.p. +48°C; dipole moment 0)

As a rule, geometrical isomers differ from one another in physical properties no less than structural isomers do. In reactions that prove their structure, geometrical isomers, however, behave in the same way, which is quite natural since their structures are identical. For example, *cis*- and *trans*-2-butenes are hydrated catalytically, giving the same compound—butane; as a result of ozonolysis, each of the isomers is converted into two molecules of acetaldehyde; under the action of HBr they both are converted into 2-bromobutane, etc.

The prefix *cis* is used for a geometrical isomer in which the like substituents (two hydrogens) are on the same side of the double bond, and the word *trans* is prefixed to an isomer in which the identical substituents are on opposite sides of the molecule. If olefinic carbon atoms are joined to four different substituents, the word *cis* or *trans* is chosen in accordance with the position of the longest chains.

cis-Isomers are easily distinguished from *trans*-isomers because the dipole moment of centrisymmetrical *trans*-isomers is equal to zero. (Further discussion of *cis-trans* isomerism is given on page 424.)

B. Preparation of Olefins

General Methods of Formation of a Double Bond in Saturated Compounds. 1. The action of sodium alkoxide or an alcoholic solution of sodium hydroxide (or other strong bases) on halogen-substituted compounds results in the elimination of a hydrogen halide and in the formation of a double bond:

$$CH_3-CH_2-CH_2Cl+NaOC_2H_5 \longrightarrow CH_3-CH=CH_2+C_2H_5OH+NaCl$$

2. Elimination of water from alcohols and other hydroxy compounds:

(a) when the vapours of these compounds are passed over alumina heated to about 400°C:

$$CH_3-CH_2-CH_2OH \xrightarrow{Al_2O_3} CH_3-CH=CH_2+H_2O$$

(b) when alcohols are heated together with sulphuric acid or non-volatile carboxylic acids, the reaction taking place via the stage of formation of an ester and its subsequent decomposition:

$$CH_3-CH_2OH+H_2SO_4 \xrightarrow[-H_2O]{} CH_3-CH_2-OSO_3H \longrightarrow CH_2=CH_2+H_2SO_4$$

$$C_3H_7OH+HO-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-OH \longrightarrow HO-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}OC_3H_7 \longrightarrow$$

$$\longrightarrow CH_3-CH=CH_2+HO-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-OH$$

3. Elimination of two halogen atoms from 1,2-dihalides by a metal (Zn, Mg):

$$R-\underset{\underset{Cl}{|}}{CH}-\underset{\underset{Cl}{|}}{CH}-R'+Zn \longrightarrow R-CH=CH-R'+ZnCl_2$$

4. The Wittig reaction which consists in the replacement of the carbonyl oxygen by a methylene group with the aid of phosphine-methylenes:

$$R-CH=O+CH_2=PR_3' \longrightarrow R-CH=CH_2+O=PR_3'$$

The Wittig reaction proceeds through the formation of an intermediate cyclic compound.

5. The replacement of the carbonyl oxygen by a methylene group not only in aldehydes, as in the Wittig reaction, but also in ketones is achieved by the action of a methylene halide and magnesium on a carbonyl compound (Cainelli, Bertini, Grasselli, 1967):

$$CH_2Br_2+\underset{\displaystyle R'}{\overset{\displaystyle R}{\overset{|}{\underset{|}{C}}}}=O+2Mg \longrightarrow \underset{\displaystyle MgBr}{\overset{\displaystyle R}{\overset{|}{\underset{|}{CH_2-C}}}}-O \longrightarrow \underset{\displaystyle R'}{\overset{\displaystyle R}{\overset{|}{\underset{|}{CH_2=C}}}}+BrMgOMgBr$$

6. Hydrogenation of compounds with a triple carbon-carbon bond over not too active a catalyst (iron partly "poisoned" with Pd or Pt):

$$R-C\equiv C-R' \xrightarrow{H_2\ (catalyst)} R-CH=CHR'$$

7. *Cracking of alkanes.* This is the principal industrial method of preparing olefins from petroleum hydrocarbons (page 92):

$$CH_3-CH_2-CH_2-CH_2-CH_3 \longrightarrow \begin{cases} \longrightarrow CH_3-CH_3+CH_3-CH=CH_2 \\ \longrightarrow CH_2=CH_2+CH_3-CH_2-CH_3 \\ \longrightarrow CH_4+CH_3-CH_2-CH=CH_2 \end{cases}$$

8. The Hofmann elimination of quaternary ammonium hydroxides has been discussed earlier (pages 287 and 288).

C. Reactions of Olefins

1. Gaseous hydrogen in the presence of active catalysts (finely divided Ni, Pd, Pt) adds on to olefins and, in general, to the multiple C=C bond, converting them to alkanes (Sabatier):

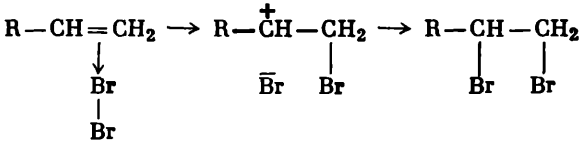
$$R-CH=CH_2 \xrightarrow{+H_2/Ni} R-CH_2-CH_3$$

2. Chlorine and bromine add on to olefins to form the corresponding 1,2-dihalides:

$$R-CH=CH_2 \xrightarrow{Br_2} R-\underset{\displaystyle Br}{\overset{|}{CH}}-\underset{\displaystyle Br}{\overset{|}{CH_2}}$$

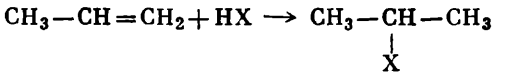
The addition of the halogens to olefins begins with the electrophilic attack on the π-bond by the halogen molecule (formation of a π-complex; see volumes III and IV). Then the halogen atom with a sextet

of electrons (i.e., positively charged) exerts an electrophilic attac on one of the carbon atoms linked by a π-bond, drawing a π-electro pair in order to form a bond with that carbon, and the partner of th latter, having lost a π-electron pair, becomes a positively charge carbonium ion and undergoes nucleophilic attack by the secon halogen atom (an anion possessing an octet of electrons):

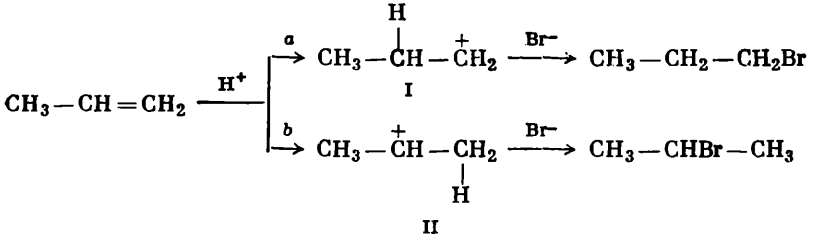


The stereochemical course and the detailed mechanism of th reaction are described in Volume II. According to this course of th reaction, propylene adds bromine twice as fast as ethylene, isobuty lene by 5.5 times faster, tetramethylethylene by 14 times faste (the inductive $+I$ effect of the CH_3 groups increases the availabilit of the electrons of the π-bond).

3. Hydrogen halides add to olefins at the multiple bond, formin alkyl halides. The reaction proceeds according to Markovnikov' rule, which predicts the direction of addition of a hydrogen halid and other polar molecules to unsymmetrically built alkenes, say, t propylene. **Markovnikov's rule** states that the hydrogen become attached to that carbon atom of the alkene which carries the larges number of hydrogen atoms, and the halogen attaches itself to th other carbon atom linked to the first one by a double bond:



The meaning of Markovnikov's rule is as follows. A hydroge halide (just as other protic acids) attacks the alkene in an electro philic manner by its proton. An unstable carbonium ion is forme as a result:



Of the two possible carbonium-ion intermediates I and II in th reaction between propylene and hydrogen bromide, the catio II with a positive charge on the secondary carbon is more stabl

(pathway *b*) because the $+I$ effect of the two methyl groups suppresses the positive charge on the central carbon more strongly than one methyl group in cation I. As a consequence, cation II is formed at a lower activation energy and hence more rapidly than cation I. The process ends with the addition of the anion Br^- to the cationic centre. All this determines the orientation of addition in accord with Markovnikov's rule.

For hydrogen bromide (but not for hydrogen chloride, acids or water) Kharasch and Mayo established in 1939 the possibility of **abnormal** or **anti-Markovnikov** addition (the direction of addition is reversed) to the double bond in the presence of a small quantity of peroxides which initiate a chain reaction by way of oxidation of hydrogen bromide to atomic bromine:

$$\left(\mathrm{RC(=O)-O-}\right)_2 + 2\mathrm{HBr} \longrightarrow 2\mathrm{RC(=O)-OH} + 2\mathrm{Br}\cdot$$

The bromine adds on to the alkene homolytically: it attacks the double bond and takes up one electron for bond formation, leaving the second electron so that the resulting transiently formed free radical has an unpaired electron on the secondary (or better, on the tertiary) but not on the primary carbon atom. Of the two directions of addition (*c* and *d*) the route *d* is realized since the structural conditions on which the stability depends are the same for carbonium ions and radicals:

$$\mathrm{CH_3-CH=CH_2} + \mathrm{Br}\cdot \longrightarrow \begin{cases} \xrightarrow{c} \mathrm{CH_3-\underset{\displaystyle Br}{\underset{|}{CH}}-\dot{C}H_2} \\ \xrightarrow{d} \mathrm{CH_3-\dot{C}H-CH_2Br} \end{cases}$$

Thus, first the atomic bromine attacks the primary carbon and the resulting free radical pulls atomic hydrogen away from HBr, again giving rise to atomic bromine and thereby initiating a new step of the chain reaction of homolytic addition:

$$\mathrm{CH_3-\dot{C}H-CH_2Br} + \mathrm{HBr} \longrightarrow \mathrm{CH_3-CH_2-CH_2Br} + \mathrm{Br}\cdot$$

$$\mathrm{CH_3-CH=CH_2} + \mathrm{Br}\cdot \longrightarrow \mathrm{CH_3-\dot{C}H-CH_2Br}$$

(chain propagation)

4. Water (in acid medium) and acids add on to olefins according to Markovnikov's rule:

$$\mathrm{CH_3-CH=CH_2} + \mathrm{H_2O} \xrightarrow{\mathrm{H^+}} \mathrm{CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3}$$

$$\mathrm{CH_3-CH=CH_2} + \mathrm{H_2SO_4} \longrightarrow \mathrm{CH_3-\underset{\displaystyle OSO_3H}{\underset{|}{CH}}-CH_3}$$

5. Hypochlorous acid adds on to alkenes also according to Markovnikov's rule if one takes into account that the positive part of the molecule is chlorine:

$$CH_3-CH=CH_2+HOCl \longrightarrow CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-\underset{\displaystyle Cl}{\underset{|}{CH_2}}$$

The same result can be achieved simply by the action of chlorine and water on an alkene:

$$CH_3-CH=CH_2+Cl_2+H_2O \longrightarrow CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-\underset{\displaystyle Cl}{\underset{|}{CH_2}}$$

It is this method that is normally employed for preparing glycol chlorohydrins.

This reaction clearly proves that the attack on an alkene by a halogen begins with the attack of the positively charged halide ion and is an electrophilic attack (of course, one of the two chlorine atoms in the symmetrically built molecule acquires a positive charge only at the moment of attack):

$$CH_3-\overset{\delta+}{C}H=\overset{\delta-}{C}H_2 \longrightarrow CH_3-\overset{+}{C}H-CH_2 + Cl^-$$
$$\quad\quad Cl-Cl \quad\quad\quad\

(2) Dichloroalkenes of the type $R-CH=CCl_2$ on conjugate chlorination in sulphuric acid containing a little water, are converted to α-chlorocarboxylic acids according to the following scheme (R. Kh. Freidlina):

$$RCH=CCl_2+Cl_2+OSO_3H^- \longrightarrow RCHCl-\underset{\displaystyle OSO_3H}{\overset{|}{C}}Cl_2+Cl^- \xrightarrow{2H_2O} RCHCl-COOH+2HCl+H_2SO_4$$

6. Addition of nitrosyl chloride:

$$CH_2=CH_2+Cl-NO \longrightarrow \underset{\displaystyle Cl}{\overset{|}{CH_2}}-\underset{\displaystyle N=O}{\overset{|}{CH_2}} \longrightarrow \underset{\displaystyle Cl}{\overset{|}{CH_2}}-\underset{\displaystyle NOH}{\overset{\|}{CH}}$$

7. Addition of N_2O_4 (N. Ya. Demyanov):

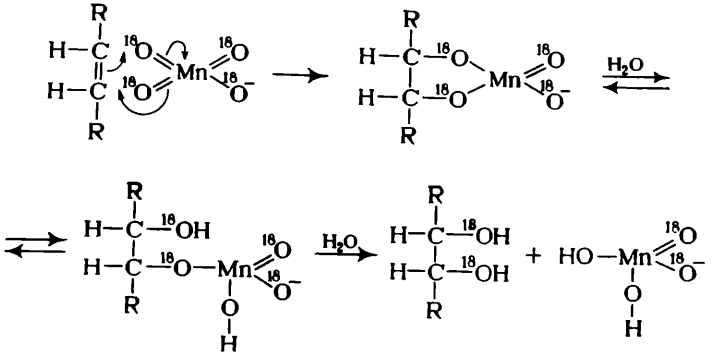
$$CR_2=CR_2+N_2O_4 \longrightarrow \underset{\displaystyle NO_2}{\overset{|}{CR_2}}-\underset{\displaystyle O-N=O}{\overset{|}{CR_2}} + \underset{\displaystyle NO_2}{\overset{|}{CR_2}}-\underset{\displaystyle NO_2}{\overset{|}{CR_2}}$$

8. Oxidation of alkenes by potassium permanganate in a weakly alkaline medium leads to the formation of glycols (the Wagner reaction):

$$CH_2=CH_2+2KMnO_4+4H_2O \longrightarrow 3\underset{\displaystyle OH}{\overset{|}{CH_2}}-\underset{\displaystyle OH}{\overset{|}{CH_2}}+2KOH+2MnO_2$$

This reaction is frequently used as a sensitive qualitative test for the detection of a multiple C=C bond.

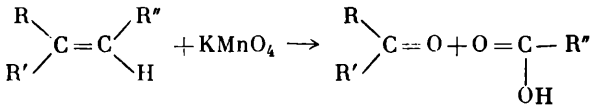
Since the oxidation of alkenes by permanganate containing heavy oxygen ^{18}O leads to the formation of oxygen-labelled glycol (MnO_4^- does not exchange oxygen with water), it is very likely that the Wagner reaction proceeds through the stage of formation of a cyclic ester:



The compound of pentavalent manganese reacts with an excess of permanganate to form the manganate MnO_4^{2-} which is then reduced to manganese dioxide.

Cyclic alkenes form *cis*-glycols by the Wagner reaction.

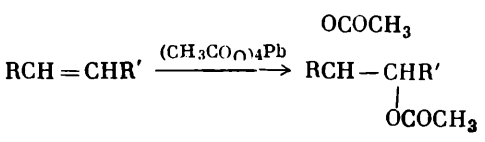
9. A more vigorous oxidation of alkenes by potassium permanganate involves the rupture of the double bond and the terminal carbon atoms form a ketonic carbonyl or carboxyl:



This reaction (as well as the one that follows) is important for elucidation of the structure of a given alkene and the position of the double bond in the chain.

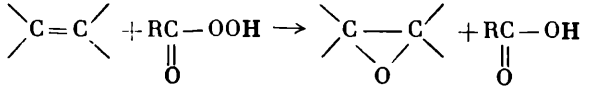
A more smooth cleavage of the double bond with the formation of two molecules of a carbonyl compound is effected by oxidation with a mixture of periodic acid and osmium tetroxide. The latter oxidizes the alkene to 1,2-glycol which is then split into two molecules of a carbonyl compound (the Malaprade reaction). The reduced osmium tetroxide is regenerated under the action of periodic acid, so that only a small amount of it need be added for the reaction to be accomplished.

10. In organic synthesis, an ever increasing use is also made of the oxidation of alkenes by lead tetraacetate in a non-aqueous medium. The reaction occurs as follows:



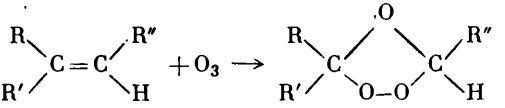
Of cycloalkenes (if R and R′ are incorporated into the ring) *trans*-diol acetates are formed.

11. Acid hydroperoxides convert alkenes quantitatively into epoxides (N. A. Prilezhaev); for example, ethylene forms the simplest epoxide—**ethylene oxide** (*epoxyethane*):

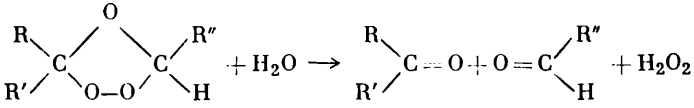


The same result is obtained when alkenes are oxidized with hydrogen peroxide (a solution in acetonitrile).

12. The reaction of ozonization introduced by Harries is important for elucidation of the structure of alkenes:

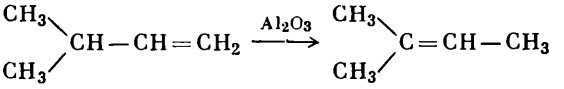


The resulting ozonides are highly unstable, explosive compounds which are decomposed by water as soon as they are formed (usually in chloroform). The decomposition reaction proceeds as folows:

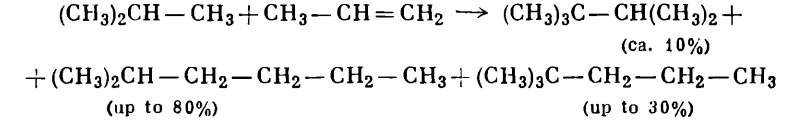


By identifying the carbonyl compounds formed, it is possible to determine the position of the double bond in the molecule and to find out whether the olefinic carbon has had hydrogen atoms (in this case an aldehyde is formed and not a ketone; when there are two hydrogen atoms per carbon atom, formaldehyde results).

13. When alkenes containing a terminal $=CH_2$ group are passed over alumina heated to a temperature above 500°C, the double bond migrates from the end of the molecule to the centre:



14. Very important are the reactions of alkylation of alkanes by alkenes, which have found wide use in the production of high-quality fuels for internal-combustion engines. The alkylation requires the use of catalysts such as $AlCl_3$, BF_3, concentrated H_2SO_4 or anhydrous HF at a low temperature. Ethylene does not enter into such reactions. Methane and ethane are not alkylated. The results of the reaction are expressed by the following scheme:



The mechanism of alkylation of an alkane by an alkene is as follows: the proton of the acid which initiates the reaction adds according to Markovnikov's rule to the alkene, in this case to propylene, forming the slightly stable carbonium ion $CH_3-\overset{+}{C}H-CH_3$ (see volume IV, "Carbonium Ions"), which pulls the hydride ion away from isobutane and gives the more stable carbonium ion $(CH_3)_3\overset{+}{C}$. The situation is complicated by the possible attack on the alkene

by the cation $CH_3-\overset{+}{C}H-CH_3$ and by the isomerization of the formed cation with transfer of the hydride ion and, consequently, of the cationic centre, so that a mixture of products is formed as a result. The carbonium ion adds on to a new molecule of the alkene, giving rise to a more complex carbonium ion:

$$(CH_3)_3\overset{+}{C}+CH_3-CH=CH_2 \longrightarrow CH_3-\overset{+}{C}H-CH_2-C(CH_3)_3$$

which becomes stabilized, abstracting the hydride ion from the new molecule of isobutane.

In this way, the heterolytic chain reaction is continued. For example,

$$CH_3-CH=CH_2+H^+ \longrightarrow CH_3-\overset{+}{C}H-CH_3$$

$$CH_3-\overset{+}{C}H-CH_3+\begin{matrix}CH_3\\ \diagdown\\ \quad CH-CH_3\\ \diagup\\ CH_3\end{matrix} \longrightarrow CH_3-CH_2-CH_3+\begin{matrix}CH_3\\ \diagdown\\ \quad \overset{+}{C}-CH_3\\ \diagup\\ CH_3\end{matrix}$$

$$\begin{matrix}CH_3\\ \diagdown\\ \quad \overset{+}{C}-CH_3\\ \diagup\\ CH_3\end{matrix}+CH_3-CH=CH_2 \longrightarrow CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_2-\overset{+}{C}H-CH_3$$

$$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_2-\overset{+}{C}H-CH_3+\begin{matrix}CH_3\\ \diagdown\\ \quad CH-CH_3\\ \diagup\\ CH_3\end{matrix} \longrightarrow$$

$$\longrightarrow CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_2-CH_2-CH_3+\begin{matrix}CH_3\\ \diagdown\\ \quad \overset{+}{C}-CH_3\\ \diagup\\ CH_3\end{matrix}, \text{ etc.}$$

15. Industrially important (as a route from propylene to butadiene and from isobutylene to isoprene) is the Prins reaction—the addition of formaldehyde in acid medium to alkenes (other aldehydes react in an analogous way):

$$CH_2=O+H^+ \rightleftharpoons \overset{+}{C}H_2-OH$$

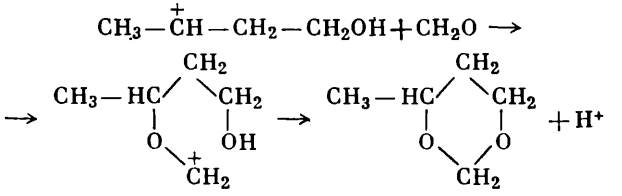
$$CH_3-CH=CH_2+\overset{+}{C}H_2-OH \longrightarrow CH_3-\overset{+}{C}H-CH_2-CH_2OH$$

The resulting carbonium ion is stabilized, depending on the conditions, either by ejection of the proton or by capture of the anion:

$$CH_3-\overset{+}{C}H-CH_2-CH_2OH \longrightarrow \begin{cases} \xrightarrow{-H^+} CH_2=CH-CH_2-CH_2OH \\ \xrightarrow{+OH^-} CH_3-CH(OH)-CH_2-CH_2OH \end{cases}$$

Both products are then easily converted into a diene.

The third way for stabilizing the carbonium ion, more common in this particular case, consists of the attack by formaldehyde and closure into a heterocyclic compound—a substituted 1,3-dioxan:



The formation of this cyclic acetal of formaldehyde could possibly be due to the action of formaldehyde on glycol (cf. page 365).

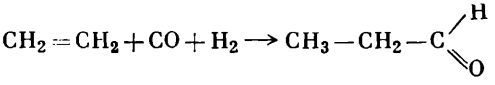
Any of the final products of the reaction may be used for synthesis of butadiene (see page 363) through the elimination of water, and in the last reaction, of formaldehyde too.

16. A second reaction that bears the name of Prins consists in adding alkyl halides or polyhaloalkanes to alkenes (better, to halogenated alkenes) under the influence of $ZnCl_2$, $FeCl_3$ or $AlCl_3$:

$$CH_2=CHCl+(CH_3)_3CCl \xrightarrow{FeCl_3} (CH_3)_3C-CH_2-CHCl_2$$

$$CCl_2=CCl_2+CCl_4 \xrightarrow{AlCl_3} CCl_3-CCl_2-CCl_3$$

17. **The oxo synthesis** of aldehydes discovered by Reppe has gained wide recognition. In this reaction, an alkene is acted on under pressure by a mixture of carbon monoxide and hydrogen in the presence of cobalt carbonyl as a catalyst (page 174):



This can, of course, be followed by the reduction of aldehydes to alcohols.

18. *Oxidation by atmospheric oxygen.* The vinyl groups of alkenes, $CH_2=CH-R$, and in particular of its various derivatives, are slowly oxidized by the oxygen of the air, which in this case causes the not yet oxidized unsaturated compound to be polymerized. The oxidation occurs by a free-radical mechanism. Apart from being polymerized (page 346), alkenes also copolymerize with the peroxide formed, so that the polymer contains a peroxide oxygen, and these peroxides serve as initiators of further polymerization processes:

$$R\bullet+O_2 \longrightarrow R-O-O\bullet$$

$$R-O-O\bullet+CH_2=CHR' \longrightarrow R-OO-CH_2-\dot{C}HR'$$

$$R-OO-CH_2-\dot{C}HR'+O_2 \longrightarrow R-OO-CH_2-\underset{\displaystyle R'}{CH}-O-O\bullet$$

$$R-OO-CH_2-\underset{\displaystyle R'}{\underset{|}{CH}}-O-O\cdot + CH_2=CHR' \longrightarrow$$

$$\longrightarrow R-OO-CH_2-\underset{\displaystyle R'}{\underset{|}{CH}}-OO-CH_2-\dot{C}HR'$$

Much faster is the oxidation of alkenes in the allylic position, i.e., across the H—C bond which is hyperconjugated (see Volume I) with the C=C bond. This results in the formation of a hydroperoxide:

$$\diagdown\!\!\diagup C=CH-CH_2R + O_2 \longrightarrow \diagdown\!\!\diagup C=CH-\underset{\displaystyle OOH}{\underset{|}{CHR}}$$

This oxidation has also a chain character and the course of the process can be represented by the following sequence of reactions:

$$R\cdot + R'CH_2-CH=CHR'' \longrightarrow$$

$$\longrightarrow RH + [R'\dot{C}H-CH=CHR'' \leftrightarrow R'CH=CH-\dot{C}HR''] \xrightarrow{O_2} R'\underset{\displaystyle OO\cdot}{\underset{|}{CH}}-CH=CHR''$$

(the radical is stabilized due to distribution of an unpaired electron)

$$R'\underset{\displaystyle OO\cdot}{\underset{|}{CH}}-CH=CHR''\cdot + R'CH_2-CH=CHR'' \longrightarrow$$

$$\longrightarrow R'\underset{\displaystyle OOH}{\underset{|}{CH}}-CH=CHR'' + R'\dot{C}H-CH=CHR'', \text{ etc.}$$

The increased rate of oxidation in the allylic position in the presence of a radical-initiator (the role of which can also be played by oxygen) is accounted for by the low activation energy of the process due to the stabilization of the allyl free radical (see also Volume IV).

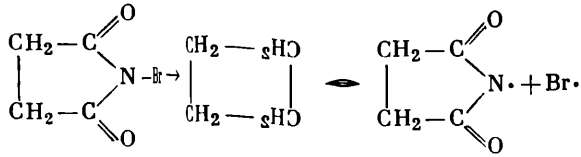
19. *Halogenation of the allylic position* (which is sometimes referred to as the α-methylenic group). At a high temperature (>500°) propylene is chlorinated in the allylic position to give allyl chloride, the double bonds remaining intact (the L'vov reaction):

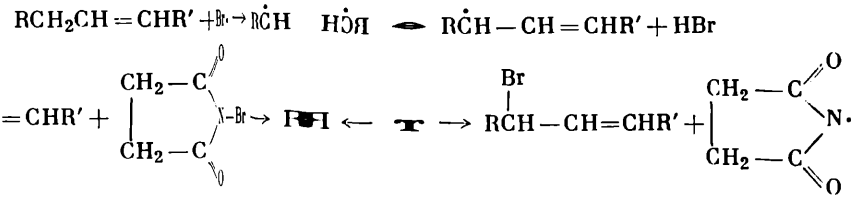
$$CH_2=CH-CH_3 + Cl_2 \xrightarrow{\text{heat}} CH_2=CH-CH_2Cl + HCl$$

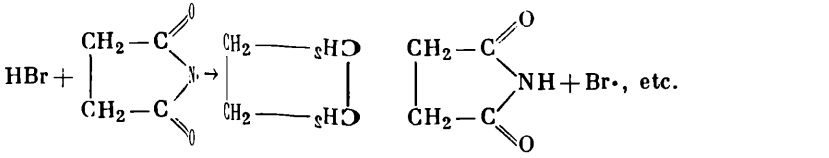
This reaction is of industrial importance in the manufacture of synthetic glycerol (page 141).

The bromination in the allyl position (discovered by Ziegler) without addition to the double bond is carried out with the aid of N-bromosuccinimide. The reaction proceeds by a chain mechanism and is initiated by compounds which generate free radicals, such

by peroxides. Since N-bromosuccinimide itself is capable of homolysis, there is no need in using another initiator:







Though the reaction is believed to be of the to be a homolytic chain process, the mechanism of the reaction cannot be considered quite indisputable.

The reactions of oxidation and halogenation at the allylic position demonstrate that the methylene group of the allyl grouping $CH=CH-CH_2-$ sharply differs in reactivity from the inert methylene group of saturated hydrocarbons and is highly susceptible to attack by radical reagents. These chain reactions take place via the formation of a free allyl radical which is much more stable than a free alkyl radical because of the possibility of the unpaired electron being distributed by the interaction with the adjacent π-bond:

$$R-CH=CH-\dot{C}H_2 \leftrightarrow R-\dot{C}H-CH=CH_2$$

Therefore, in order to abstract the hydrogen atom from the allyl position, a lower amount of energy is needed than in the case of the abstraction of a hydrogen atom from from an alkane.

Such a distribution is also possible for a pair of electrons (a negative charge) in the allyl position:

$$RCH=CH-\ddot{C}H_2 \leftrightarrow R\ddot{C}H-CH=CH_2$$

Therefore, not only atomic hydrogen but also a proton is expelled from the allyl position more easily than from alkanes.

20. *Oxidative ammonolysis.* When alkenes are oxidized by oxygen in the presence of ammonia over a heterogeneous catalyst*, nitriles are formed. For instance, propylene gives acrylonitrile:

$$CH_3-CH=CH_2+NH_3+\frac{3}{2}O_2 \xrightarrow{\text{catalyst}} CH_2=CH-C\equiv N+3H_2O$$

21. *Polymerization of alkenes.* This process was discovered by Butlerov who carried out the di- and trimerization of isobutylene or isobutene (2-methyl-1-propene) in the presence of sulphuric acid. The process consists of the addition of one molecule of the alkene to be dimerized to another at the expense of the "allyl" hydrogen. In an acid medium the addition product is partially isomerized with transfer of the double bond to the centre of the molecule, as a result of which a mixture of two products is obtained:

$$2\ \begin{matrix}CH_3\\ \\ CH_3\end{matrix}\!\!\diagdown\!\!C=CH_2 \longrightarrow CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}}-CH_2-\underset{}{\overset{\displaystyle CH_3}{\overset{|}{C}}}=CH_2+CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}}-CH=\overset{\displaystyle CH_3}{\overset{|}{C}}-CH_3$$

Both dimers on catalytic hydrogenation form 2,2,4-trimethylpentane (isooctane)—a fuel with an octane number of 100 (page 90), and that is why this process is carried out on a large industrial scale.

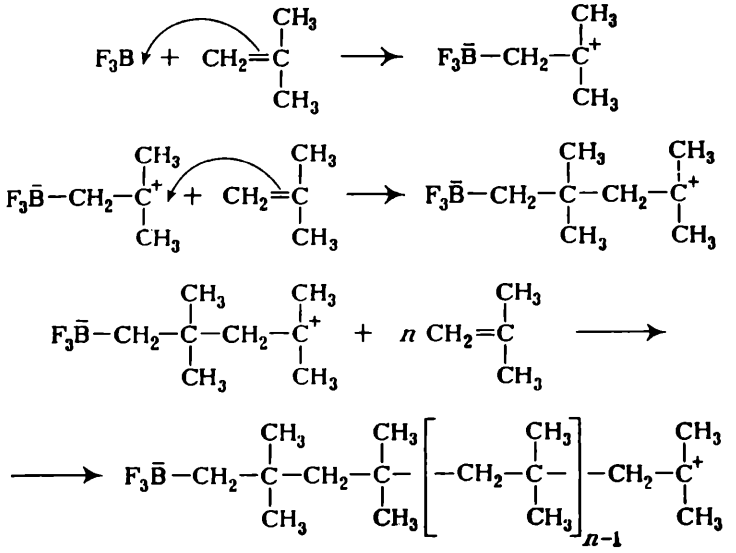
Triisobutylene is a mixture of isobutylene trimers of different structure, which are made by addition of the above-mentioned dimers to isobutylene.

Especially important is the polymerization of the lower alkenes (ethylene and propylene) resulting in the formation of high polymers with a molecular weight of 10^4-10^5 and higher. The first industrial polymerization was that of isobutylene to Oppanol (German trademark) or Vistanex (USA trademark). The polymerization was carried out at a very low temperature (about —100°C) in the presence of boron trifluoride (heterolytic polymerization), examples of which we have already studied on formaldehyde.

Lewis acids (BF_3, $AlCl_3$) and the hydrogen ion are all initiators of the heterolytic (more exactly, cationic) polymerization. These initiators abstract an electron pair from the π-bond to make up for the electron deficiency (for bond formation, hydrogen may accept a pair of electrons and the hydrogen ion has no electrons; the elements of Group III have a tendency to supplement the sextet of electrons in order to achieve an octet). The molecule of an alkene assumes a positive charge on the second olefinic carbon (carbonium

* A wide range of catalysts has been patented, say, phosphomolybdenic salts of bismuth, antimony, and tin.

ion), which abstracts a pair of electrons from the next alkene molecule, thereby continuing the polymerization chain:



The chain is growing until a random encounter with an anion terminates it. In the resulting high-molecular compound with a molecular weight of several hundreds of thousands, the number of initiator molecules at one end of the chain and the number of anions terminating the chain at the other end are vanishingly small and cannot be detected in a quantitative analysis of ordinary accuracy. Because of the small content, their presence does not affect the properties of the compound, which are entirely determined by the properties of the paraffinic chain. With such too high molecular weights, polymers with linear molecules display elastic properties (see Sec. 3.7). For instance, Oppanol is a chemically stable (in contrast to natural rubber) elastic material.

The most readily polymerizable are alkenes which have the group $\rangle C{=}CH_2$ at the end and are built unsymmetrically. Ethylene is polymerized with difficulty and its polymerization was carried out later (Dinzes) but soon found industrial application. The polymerization of ethylene was first effected by compressing it up to about 1000 kg/cm^2 in the presence of traces of oxygen and by heating. This kind of polymerization is also a chain process, though a homolytic but not a heterolytic one. The initiator of the homolytic polymerization (oxygen in this particular case, but any other free radical with an unpaired electron, say, $CH_3\cdot$, may also be used) pulls one of the

electrons of the π-bond, thus converting the second carbon atom into a free-radical carbon*:

$$\cdot O-O\cdot \overset{\curvearrowright}{CH_2=CH_2} \overset{\curvearrowleft}{} \longrightarrow \cdot O-O-CH_2-CH_2\cdot$$

$$\cdot O-O-CH_2CH_2\cdot + CH_2=CH_2 \rightarrow \cdot O-O-CH_2CH_2CH_2CH_2\cdot$$

$$O-O-CH_2CH_2CH_2CH_2\cdot + nCH_2=CH_2 \rightarrow \cdot O-O-CH_2CH_2CH_2CH_2(CH_2CH_2)n\cdot$$

The chain grows until a random encounter with a particle bearing alone electron (an oxygen molecule, a similar particle, a free radical) stops the chain growth. What has been said about the vanishingly small role of the end groups in such enormous molecules where the properties are governed by the character of the chain remains valid in this case. The thus obtained polyethylene (polythene) is a solid horny mass which becomes soft at a temperature of about 120°C and has a molecular weight of 18,000-50,000, is mechanically strong, and chemically inert, like paraffin wax. Polyethylene is widely used as an electrical insulator, and for making kitchenware, and packaging and greenhouse films, etc.

Polyethylene of this type has nevertheless a certain number of branchings in the macromolecule, which are formed as a result of a hydrogen atom being pulled randomly from the chain by the free-radical end of another growing chain:

$$\ldots -CH_2CH_2CH_2CH_2- \ldots + \cdot CH_2CH_2- \ldots \longrightarrow$$

$$\longrightarrow \ldots -CH_2CH_2\dot{C}HCH_2- \ldots + CH_2=CH_2 \longrightarrow$$

$$\longrightarrow \ldots -CH_2CH_2CHCH_2- \ldots \text{ and so on}$$

$$CH_2CH_2\cdot$$

In the 50's of this century Ziegler discovered a process for preparing polyethylene with unbranched chains, which has also found wide use. The process involves the action of triethylaluminium on ethylene. Thus, triethylaluminium adds on to alkenes; this property is also displayed by the trialkylaluminium resulting from the addition of an alkene:

$$al C_2H_5 + CH_2=CH_2 \longrightarrow al CH_2CH_2CH_2CH_3$$

$$al CH_2CH_2CH_2CH_3 + CH_2=CH_2 \longrightarrow al CH_2CH_2CH_2CH_2CH_2CH_3, \text{ etc.}$$

where *al* represents one-third of an aluminium atom.

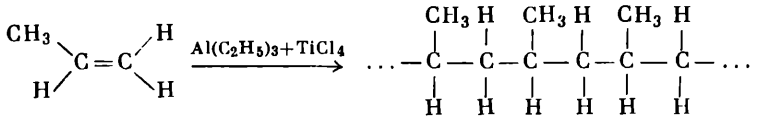
The subsequent hydrolysis gives pure polyethylene:

$$al CH_2CH_2(CH_2CH_2)_nCH_2CH_3 \xrightarrow{H_2O} al(OH) + CH_3CH_2(CH_2CH_2)_nCH_2CH_3$$

When $TiCl_4$ is added to triethylaluminium, the polymerization

* The dashed arrows signify the transfer of one electron.

proceeds especially well and has a specific feature in that **isotactic** polymers are obtained from unsymmetrical alkenes. For example, propylene gives isotactic polypropylene in which all the side groups (CH_3 in this case) occupy identical spatial positions:



Owing to this, the chains of an isotactic polymer pack together more tightly and the polymer obtained is stronger. Polypropylene of this type is so strong that it is used for the manufacture of synthetic fibres.

Isotacticity is a stereochemical concept and will be discussed in more detail in Volume II.

From the chemical standpoint, all these high-molecular-weight compounds (polyethylene, polypropylene, Oppanol) belong to the class of paraffinic hydrocarbons (alkanes) with properties that we have studied earlier.

D. Uses of Olefins

Owing to their availability (cracking of petroleum) and to their high and versatile reactivity, alkenes serve today as the chief raw material (together with aromatic hydrocarbons and acetylene) for the various numerous branches of industrial organic chemistry.

An ever increasing quantity of ethylene is used for the production of polyethylene. The amount of ethylene being hydrated to ethanol (page 128) is also increasing. The conversion of ethylene into ethylene oxide by atmospheric oxygen or via ethylene chlorohydrin and further syntheses of acetaldehyde, ethylene glycol (an antifreeze), its ethers and esters (solvents), ethanolamines on the basis of ethylene oxide (page 158 *et seq.*) constitute the major section of the chemical industry.

Propylene together with isobutylene has found its way into the production of hydrocarbon additives (alkylation) which increase the octane number of motor fuels; the uses of propylene include the preparation of secondary propyl alcohol, acetone, acrylonitrile. Ever increasing amounts of propylene are used in the production of polypropylene.

The dehydrogenation of the butylenes $CH_3—CH_2—CH=CH_2$ and $CH_3—CH=CH—CH_3$ over the catalyst Cr_2O_3 at 500°C or above yields butadiene which is then converted into synthetic rubber (page 380).

Isobutylene, $(CH_3)_2C=CH_2$, is subjected to dimerization and subsequent hydrogenation to synthesize isooctane, which is used as an additive to motor fuels to raise their octane number.

Isobutylene is also used for preparing polyisobutylene (polyisobutene) and in the production of *tert*-butyl alcohol.

3.2. Acetylenes (Alkynes)

The nature of the triple bond characteristic of acetylene and its homologues has already been discussed (pages 320 and 330).

The general formula of the hydrocarbons of the alkyne series is C_nH_{2n-2}. The simplest member of this series is **acetylene**, $CH \equiv CH$, and the class as a whole is frequently referred to as the **acetylenes**. The trivial or common names of the homologues of acetylene are built by adding the names of the radicals that replace hydrogens to acetylene: methyl-acetylene, $CH_3—C\equiv CH$; dimethylacetylene, $CH_3—C\equiv C—CH_3$; methylethylacetylene, $CH_3—C\equiv C—C_2H_5$. According to the IUPAC system, acetylene is called **ethyne**, and the names of its homologues are derived from the name of the corresponding, completely saturated hydrocarbon (alkane) by changing the suffix *-ane* to *-yne* with indication of the number of the carbon atom (according to the IUPAC rules of numbering) from which the triple bond originates. Examples are given in Table 3.2 which also presents the physical properties of some of the acetylenic hydrocarbons. The radical of acetylene $HC\equiv C—$ is called **ethynyl.**

A. Preparation of Alkynes

Preparation of Acetylene. Acetylene is produced on an extensive commercial scale.

1. Until recently the main source of acetylene has been calcium carbide which is obtained by heating a mixture of quicklime and coke in an electric furnace to a temperature higher than 2500°C:

$$CaO + 3C \longrightarrow CaC_2 + CO$$

Acetylene is prepared through the decomposition of calcium carbide by water:

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + HC \equiv CH$$

The method was discovered as far back as 1862 by Wöhler and has retained its value up to the present time.

The major proportion of acetylene used for metal welding is now produced by this method. The main disadvantage of the carbide method is its high energy consumption.

2. Preparation of acetylene by pyrolysis of hydrocarbons. The starting materials are gaseous saturated hydrocarbons, chiefly readily available methane or liquid petroleum fractions—straight-run gasolines, kerosene.

The **pyrolysis** of methane (electrical or thermal) is effected by heating the gas up to 1400°C. It leads to the formation of an acetylene-hydrogen mixture:

$$2CH_4 \longrightarrow HC \equiv CH + 3H_2$$

The reaction is endothermic (95 kcal/mole) and the electrical pyrolysis is therefore only slightly more economical in the consumption of electrical energy than the carbide process used for the production of acetylene.

In **oxidative pyrolysis** with addition of a limited amount of air, part of methane is burned and part of it is pyrolysed by the heat evolved. The yield of acetylene amounts to 15 per cent. It is isolated from a mixture of gases by taking advantage of its rather high solubility in water as compared with other hydrocarbons.

The pyrolysis of methane is accomplished on a large industrial scale and is at present the most important method of acetylene production.

The pyrolysis of liquid hydrocarbons at 1200-1500°C leads to the formation of acetylene more readily than the cracking of methane. In particular, a method has been suggested for preparing acetylene from kerosene by exposure to an electric arc under a layer of liquid.

3. Acetylene was discovered by Edmund Davy (1836) in illuminating gas in which it is present in a small amount and is evidently formed as a result of the cracking of hydrocarbons.

4. Synthesis of acetylene from the elements. By passing an electric arc between carbon electrodes in an atmosphere of hydrogen, Berthelot prepared acetylene (an endothermic process: about 55 kcal/mole). This method has no practical value but is important historically.

Synthesis of Acetylenic Hydrocarbons (methods of formation of the triple C≡C bond in the chain of carbon atoms).

1. *Based on olefins.* A halogen molecule is added to an alkene R—CH=CH—R′ and the resulting dihalide is acted on by an alcoholic solution of sodium hydroxide to split off two molecules of HHal (Savich):

$$RCHCl—CHClR' + 2NaOH \longrightarrow RC \equiv CR' + 2NaCl + 2H_2O$$

2. *Based on ketones.* A ketone is reacted at 150-170°C with phosphorus pentachloride, the oxygen being replaced by two chlorine atoms and, just as in the preceding method, two molecules of HCl being elimina-

TABLE 3.2. **Acetylenes or Alkynes**

Formula	Name			m.p., °C	b.p., °C	Density
	trivial	IUPAC	acetylenic system			
$CH \equiv CH$	Acetylene	Ethyne	Acetylene	−81.8	−83.6 (subl.)	0.6200 (d_4^{-84})
$CH_3-C \equiv CH$	Allylene	Propyne	Methylacetylene	−104.7	−23.3	0.6785 (d_4^{-27})
$C_2H_5-C \equiv CH$	Crotonylenes	1-Butyne	Ethylacetylene	−130.0	−8.6	0.6680 (d_4^0)
$CH_3-C \equiv C-CH_3$		2-Butyne	Dimethylacetylene	−32.3	27.2	0.6880 (at 25°C)
n-$C_3H_7-C \equiv CH$	Valerylenes	1-Pentyne	n-Propylacetylene	−95	40.0	0.6882 (d_4^{25})
$CH_3-C \equiv C-C_2H_5$		2-Pentyne	Methylethylacetylene	−101	56.0	0.7127 (at 17.2°C)
$(CH_3)_2CH-C \equiv CH$		3-Methyl-1-butyne	Isopropylacetylene	−89.7	29.3	0.6854 (d_4^0)

ted by an alcoholic solution of sodium hydroxide (A. E. Favorsky):

$$R-\underset{\underset{O}{\|}}{C}=CH_2R' \xrightarrow{PCl_5} R-\underset{Cl}{\overset{Cl}{C}}-CH_2R' \xrightarrow[-2HCl]{2NaOH} RC\equiv CR'$$

3. The use of the Iotsich reagent (page 358). The alkylation of organomagnesium derivatives of acetylene yields its homologues.

4. The electrolysis of substituted fumaric acids (page 422) leads to substituted acetylenes:

$$^-OOC-CR'=CR''-COO^- \xrightarrow{2e} R'C\equiv CR''+2CO_2$$

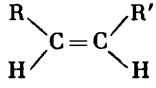
B. Reactions of the Triple Carbon-Carbon Bond

The triple bond is similar in reactivity to the double bond but is not superior to it in activity. Addition reactions characteristic of multiple bonds occur in two stages for the triple bond. Examples of such additions will be given later.

1. *Addition of hydrogen.* Nascent hydrogen does not react with the triple bond (as well as with the double bond), but gaseous hydrogen in the presence of active catalysts (Ni, Pt) instantly reduces alkynes to alkanes:

$$RC\equiv CR' \xrightarrow{H_2/Ni} RCH_2-CH_2R'$$

The first stage of this reaction (the reduction to alkenes) can also be effected by using a less active catalyst (palladium "poisoned" with $PbCO_3$, Raney nickel). This results in *cis*-olefins:

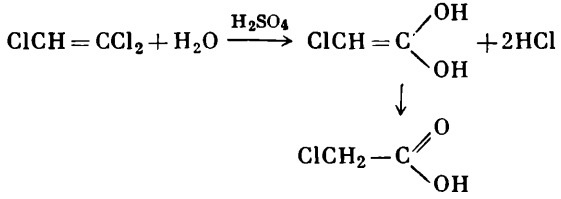


2. *Addition of chlorine and bromine.* The reaction involves two distinct stages, the first stage (*trans*-addition) proceeding more vigorously:

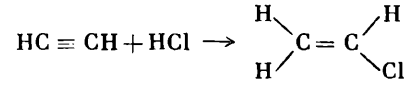
$$R-C\equiv C-R' \xrightarrow{Cl_2} \underset{Cl}{\overset{R}{C}}=\underset{R'}{\overset{Cl}{C}} \xrightarrow{Cl_2} RCCl_2-CCl_2R'$$

With an insufficient amount of chlorine acetylene forms dichloroethylene (1,2-dichloroethene, ClCH=CHCl), and in the presence of excess chlorine, tetrachloroacetylene (1,1,2,2-tetrachloroethane, $Cl_2CH-CHCl_2$) is formed. In industry, HCl is eliminated from tetrachloroethane by the action of alkalis (lime) and an important solvent—trichloroethylene, $ClCH=CCl_2$, is produced, the hydrolysis

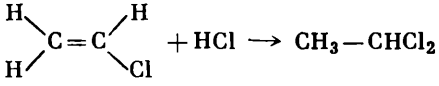
of which under the action of sulphuric acid gives monochloroacetic acid:



3. The addition of a hydrogen halide involves two distinct stages. For example, when HCl is added to acetylene at the first stage, vinyl chloride is obtained:



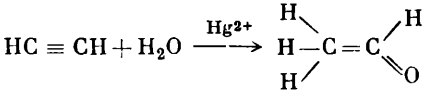
This is one of the industrial methods of preparing vinyl chloride in enormous quantities (page 389). The second hydrogen halide molecule adds on according to Markovnikov's rule (page 336) with the formation of an ethylidene halide (1,1-dichloroethane):



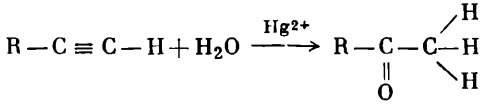
Vinyl bromide and ethylidene bromide are formed in an analogous way. The addition of hydrogen bromide contrary to Markovnikov's rule is unknown in this case.

4. The acetylenic multiple bond is oxidized by permanganate and ozonized.

5. In the presence of catalysts (the Hg^{2+} ion) acetylenes add on water in accordance with Markovnikov's rule, acetaldehyde being obtained from acetylene:



and ketones from its homologues:



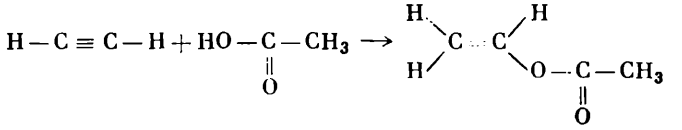
The first of these two reactions is an industrially important process because it is employed to produce the major proportion of acetaldehyde, which is further converted into acetic acid (M. G. Kuchorov), ethanol and a large variety of other products.

6. Under the catalytic effect of potassium hydroxide, acetylene and acetylenes of the type RC≡CH being subjected to a pressure of several atmospheres add on alcohols, this leading to **alkylvinyl esters** (A. Favorsky, M. Shostakovsky; W. Reppe):

$$CH \equiv CH + ROH \xrightarrow{KOH} RO-CH=CH_2$$

The reaction is carried out on an industrial scale. Mercaptans react with acetylenes in a similar way.

7. Under the conditions of heterogeneous catalysis (H_3PO_4 or B_2O_3) acetylene adds on acetic acid, forming a complex vinyl ester—**vinyl acetate**:



Vinyl acetate is an important starting material for polymerization into polyvinyl acetate which is hydrolysed to polyvinyl alcohol (page 391).

8. Acetylene adds on the chlorides of some metals:

$$HC \equiv CH + HgCl_2 \longrightarrow ClCH=CHHgCl$$

$$HC \equiv CH + AsCl_3 \xrightarrow{HgCl_2} \underset{\text{Lewisite}}{ClCH=CHAsCl_2}$$

$$HC \equiv CH + SbCl_5 \longrightarrow (ClCH=CH)_3SbCl_2$$

These reactions have not yet been studied for the homologues of acetylene.

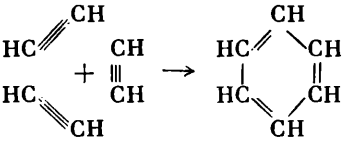
Exceedingly important are the reactions of polymerization of acetylene.

9. With cuprous and ammonium chlorides in acid solution acetylene undergoes linear dimerization to **vinylacetylene** and is trimerized to **divinylacetylene** (Nieuwland):

$$HC \equiv CH \longrightarrow \begin{cases} CH_2=CH-C \equiv CH \\ CH_2=CH-C \equiv C-CH=CH_2 \end{cases}$$

Divinylacetylene is isomeric with benzene (see Volume IV). The process is carried out industrially for production of vinylacetylene, from which synthetic chloroprene rubber is made (page 374). In some countries, vinylacetylene is subjected to partial hydrogenation to prepare butadiene for the production of ordinary butadiene rubber (page 365).

10. The long-known trimerization of acetylene (Berthelot, 1866) on prolonged heating up to 400-500°C gives benzene in low yield:

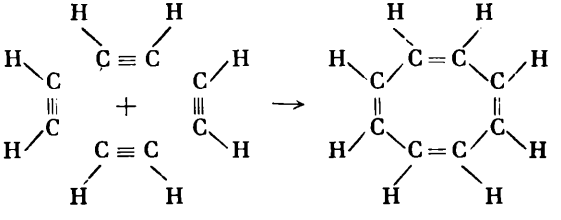


N. D. Zelinsky and B. A. Kazansky modified this reaction: acetylene is passed at about 600°C over activated charcoal as a catalyst. This reaction gives benzene and other aromatic hydrocarbons, especially naphthalene, in good yield.

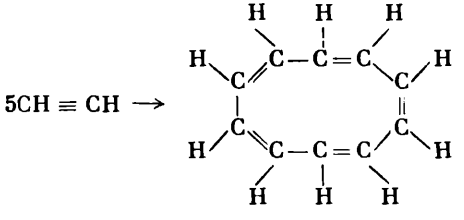
Substituted acetylenes trimerize with good yield to substituted benzenes under the action, say, of $[(C_6H_5)_3P]_2[Ni(CO)]$ or certain complex chromium salts at room temperature.

11. The oldest process of polymerization of acetylene into a high-molecular-weight product consists in passing acetylene over metallic copper at 200-300°C. This reaction leads to so-called **cuprene** of variable composition, $(C_2H_2)_x$, which is an insoluble, yellowish, flocculent powder or a cork-like solid, whose structure has not yet been finally established.

12. A remarkable discovery made by Reppe is the **tetramerization** of acetylene (and its pentamerization) into **cyclooctatetraene** and **cyclodecapentaene** in tetrahydrofuran solution at a pressure of about 20 kg/cm^2. The catalyst used is nickel cyanide or nickel acetylide:



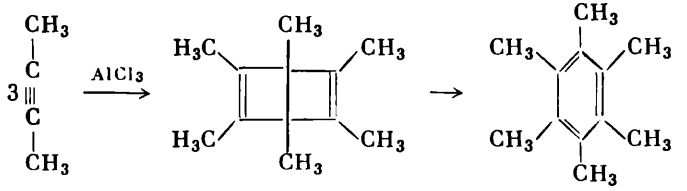
Cyclooctatetraene



Cyclodecapentaene

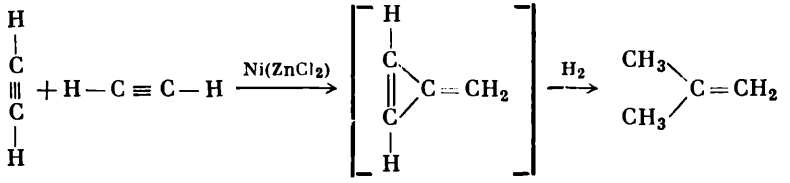
13. In 1966 Schaeffer found that a benzene solution of dimethylacetylene when allowed to stand over aluminium chloride trimerizes

into hexamethylbicyclo[2,2,0]hexadiene (Dewar hexamethylbenzene), which in its turn isomerizes on heating into **hexamethylbenzene.**



Hexamethylbenzene is made directly from dimethylacetylene over a catalyst—cobalt dimesitylene (see Volume III).

14. The hydrogenation of acetylene over nickel in the presence of zinc chloride yields isobutylene, it is believed that a dimer of the structure given below is formed as an intermediate by "cross dimerization" (A. D. Petrov):



15. In the presence of nickel carbonyl, $Ni(CO)_4$, and the carbonyls of other metals acetylene adds on carbon monoxide and water or alcohol, forming **acrylic acid** or its ester (Reppe):

$$H-C\equiv C-H+CO+ROH \longrightarrow CH_2=CH-\underset{\underset{O}{\|}}{C}-OR$$

This is an important industrial process.

16. Under the action of a catalyst ($CuCl_2 + NH_3$) acetylene adds on hydrocyanic acid to give **acrylonitrile:**

$$HC\equiv CH+HCN \longrightarrow CH_2=CH-C\equiv N$$

This is one of the three most significant industrial methods for synthesis of acrylonitrile (page 412) which is of great value in the industry of organic compounds.

C. Reactions of Substitution of Hydrogen Atoms of Acetylene

The hydrogen atoms of acetylene and of the acetylenes of the structure RC≡CH, attached to the triply bound carbon atom can easily be abstracted as a proton.*

* Another well-known example of replacement of such hydrogen atoms is provided by the acidic properties of hydrocyanic acid, H—C ≡ N.

1. The interaction of acetylene (and RC≡CH) with ammoniacal solutions of silver oxide or cuprous chloride gives precipitates of insoluble acetylides—colourless silver acetylide ($AgC{\equiv}CAg$) and coloured copper acetylides whose colour ranges from cherry-brown ($CuC{\equiv}CCu$) to yellow-brown ($RC{\equiv}CCu$). These acetylides are explosive compounds:

$$HC{\equiv}CH + 2[Ag(NH_3)_2]^+OH^- \longrightarrow AgC{\equiv}CAg + 4NH_3 + 2H_2O$$
$$RC{\equiv}CH + [Ag(NH_3)_2]^+OH^- \longrightarrow RC{\equiv}CAg + 2NH_3 + H_2O$$
$$HC{\equiv}CH + 2[Cu(NH_3)_2]^+OH^- \longrightarrow CuC{\equiv}CCu + 4NH_3 + 2H_2O$$
$$RC{\equiv}CH + [Cu(NH_3)_2]^+OH^- \longrightarrow RC{\equiv}CCu + 2NH_3 + H_2O$$

2. Under the action of an alkylmagnesium halide the hydrogen abstracted as a proton combines with the alkyl radical, forming an alkane, and the hydrogen atom is replaced by the residue MgHal:

$$HC{\equiv}CH + 2CH_3MgI \longrightarrow IMgC{\equiv}CMgI + 2CH_4$$
$$RC{\equiv}CH + CH_3MgI \longrightarrow RC{\equiv}CMgI + CH_4$$

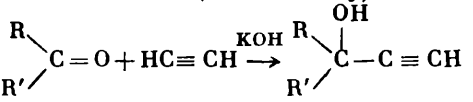
3. In a solution of metallic sodium in liquid ammonia the mobile hydrogen of acetylene is replaced by a sodium atom:

$$HC{\equiv}CH + Na(NH_3) \longrightarrow HC{\equiv}CNa + NH_3 + {}^1/_2H_2$$
$$HC{\equiv}CH + 2Na(NH_3) \longrightarrow NaC{\equiv}CNa + 2NH_3 + H_2$$
$$RC{\equiv}CH + Na(NH_3) \longrightarrow RC{\equiv}CNa + NH_3 + {}^1/_2H_2$$

The derivatives of magnesium (the Iotsich reagent) and sodium are widely employed in organic synthesis; they behave as a Grignard reagent (page 128).

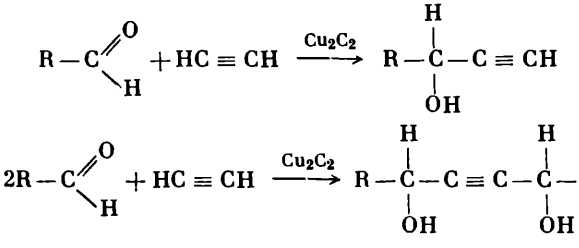
The increased mobility of a hydrogen atom is manifested also in a number of condensation reactions involving acetylene, which are of importance in laboratory and industrial syntheses.

4. In the presence of potassium hydroxide, acetylene (under a low pressure) reacts with ketones (A. Favorsky):



In this way, tertiary alcohols with an ethynyl radical are obtained.

5. In the presence of cuprous acetylide, acetylene adds on to aldehydes (Reppe):



Especially important is the addition of acetylene to formaldehyde, which leads to propargyl alcohol, $HC{\equiv}CCH_2OH$ or to 1,4-butynediol:

$$HC \equiv CH + 2HC\begin{matrix} H \\ \diagdown\!\!\!\!\diagup \\ O \end{matrix} \xrightarrow{Cu_2C_2} HOH_2C-C \equiv C-CH_2OH$$

which is a starting material in the industrial synthesis (FRG) of tetrahydrofuran and butadiene (see page 364).

6. The Favorsky acetylene-allene-diene rearrangement. When acetylenes with the triple bond remote from the end are heated with metallic sodium, the triple bond migrates to the extreme position:

$$R-C \equiv C-CH_3 \xrightarrow{Na} R-CH_2-C \equiv CH$$

and when acetylenes with the triple bond in the extreme position are heated with alkali, the bond migrates to the centre of the molecule:

$$R-CH_2-C \equiv CH \xrightarrow{C_2H_5ONa} R-C \equiv C-CH_3$$

The reaction evidently consists in the following: the alkoxide ion expels a proton from the CH_2 group adjacent to the triple bond and the free electron pairs of the C—H bonds form successively two new π-bonds between the third (in this particular case) and the second carbon atom, forcing the electron pairs of the former π-bonds to move to the extreme carbon atom which accepts protons from the reaction medium for these pairs:

$$R-\overset{3}{C}H-\overset{2}{C}{\equiv}CH \longrightarrow R-CH=C=\ddot{C}H \xrightarrow{H^+} R-CH=C=CH_2$$

(H and OC_2H_5 attached to the third carbon)

$$R-C{\equiv}C=CH_2 \longrightarrow R-C{\equiv}C-\ddot{C}H_2 \xrightarrow{H^+} R-C{\equiv}C-CH_3$$

(H and OC_2H_5 attached to the third carbon)

If the third carbon atom has only one hydrogen, the reaction ends at the first stage and acetylene is converted into a diene—a substituted allene (page 360) which is capable of further rearrangement into a diene with conjugated double bonds (see page 363).

D. Acetylene

From the foregoing it is seen that acetylene occupies an eminent position among the members of the alkyne series: it is of great technical importance and has been thoroughly studied. Apart from acetylene and vinylacetylene, one can hardly cite an acetylenic hydrocar-

bon which is of any industrial importance. The world output of acetylene amounts to millions of tons. The greater portion of acetylene is used for welding and cutting of metals since the acetylene-oxygen flame has an extremely high temperature (up to 2800°C) and melts steel easily. This application of acetylene is associated not so much with its endothermic nature (—55 kcal/mole) as with the low heat capacity of the combustion products (little water is formed). Indeed, the combustion of ethane liberates 373 kcal/mole, which in terms of 1 gram is almost the same as the amount of heat evolved upon the combustion of acetylene (311 kcal/mole). The endothermic nature of acetylene is responsible for an explosion upon compression. At a low pressure (15 kg/cm^2) acetylene is excellently soluble in acetone (300 volumes of gas in 1 volume of liquid) and is not dangerous when dissolved in acetone. Cylinders in which acetylene dissolved in acetone is supplied for use are packed with an inert porous material to cut down on the free volume. Mixtures of acetylene with air are explosive in wide limits.

Carbide acetylene has a nauseating smell due to the impurities present in it. Pure acetylene has an odour typical of unsaturated hydrocarbons and has a narcotic effect, for which reason it finds application in surgery as an anesthetic (narcylene).

The chemical industrial applications of acetylene are many and varied and are due to the reactions indicated above. Acetylene is especially extensively used in industrial synthesis in countries which have no petroleum of their own. It is used as the starting material for the production of the simplest key compounds for basic organic synthesis (acetaldehyde, ethanol, acetic acid, halogen derivatives of ethylene, chloroacetic and trichloroacetic acids) and also the following chemical end products—synthetic rubbers, plastics, etc.

3.3. Dienes (Diolefins)

Unsaturated hydrocarbons containing two carbon-carbon double bonds are isomeric with the acetylenes of the corresponding skeleton and have the same general formula C_nH_{2n-2}. According to the IUPAC system, their names are formed by adding the ending *—diene*: propadiene, butadiene, pentadiene, etc. The trivial (common) and IUPAC names of certain dienes and their physical properties are given in Table 3.3.

Dienes differ in methods of preparation and particularly in properties, depending on the relative position of double bonds.

Hydrocarbons of the type $RCH=C=CH_2$ are called **allenes** after the name of the first member of the series—allene, $CH_2=C=CH_2$. This system of double bonds is called **cumulated double bonds**. The

TABLE 3.3. **Hydrocarbons with Two Ethylenic Bonds (Dienes)**

Formula	Name		m.p., °C	b.p., °C	Density d_4^{20}	Refractive index n_D^{20}
	trivial	IUPAC				
$CH_2=C=CH_2$	Allene	Propadiene	−146.0	−32.0	1.787	—
$CH_3-CH=C=CH_2$	Methylallene	1,2-Butadiene	−136.3	+10.8	0.676 (d_4^0)	1.4205
$CH_2=CH-CH=CH_2$	Divinyl	1,3-Butadiene	−108.9	−3.0	0.650 (d_4^{-6})	1.4292 (at −25°C)
$CH_3-CH=CH-CH=CH_2$	Piperylene	1,3-Pentadiene (*trans*-)	−87.5	+43.0	0.683	1.4301
$CH_2=C(CH_3)-CH=CH_2$	Isoprene	2-Methyl-1,3-butadiene	−145.9	34.0	0.681	1.4194
$CH_2=C(CH_3)-C(CH_3)=CH_2$	Diisopropenyl	2,3-Dimethyl-1,3-butadiene	−76.1	69.6	0.745 (d_0^0)	1.4377
$(CH_3)_2C=CH-CH=C(CH_3)_2$	Diisocrotyl	2,5-Dimethyl-2,4-hexadiene	−91.3	102.5 (756 mm Hg)	0.716 (d_4^{21})	1.4781
$CH_2=CH-CH_2-CH=CH_2$	Divinylmethane	1,4-Pentadiene	−148.3	25.9	0.661	1.3888
$CH_2=CH-CH_2-CH_2-CH=CH_2$	Diallyl	1,5-Hexadiene	−140.7	59.6	0.688	1.4040

specific feature of cumulated double bonds is that the central carbon atom, which carries two double bonds, is in the third valence state and, hence, all the three carbon atoms of allene lie in a single straight line, the two extreme carbon atoms are in the second valence state.

The most specific and most important dienes are 1,3-dienes. The first representative of this group of dienes is 1,3-butadiene, $CH_2=CH-CH=CH_2$. All the four carbon atoms of 1,3-butadiene are in the second valence state, and the 1,3 arrangement of the double bonds is termed **conjugated** because in addition reactions the entire system often behaves as an entity, as will be shown later. The bond conjugation in 1,3-butadiene (and in other conjugated systems) affects the energy level of the system, which is 3-4 kcal/mole lower than in systems with isolated double bonds. This is seen from the fact that the catalytic hydrogenation of olefins liberates 30 kcal/mole and the hydrogenation of 1,3-butadiene liberates not 60, as in the case of dienes with isolated π-bonds, but 56.4 kcal/mole. Thus, the conjugation decreases the energy of two double bonds by a factor of 3.6 kcal/mole (the conjugation effect or the resonance energy).

The essence of the effect is as follows. The *p*-electron clouds that form two π-bonds overlap not only between the first and the second carbon atom and, accordingly, between the third and the fourth, but also between the second and the third carbon atom, forming the entire system. The 2,3-overlap is not just as complete as the 1,2- and 3,4-overlaps, as evidenced from the X-ray measurements of the distances between the carbon atoms: the distances between the carbons 1-2 and 3-4 are equal to 1.37 Å and the distance between the carbon atoms 2-3 is somewhat greater (1.46 Å), though smaller than the normal length of the C—C bond in saturated hydrocarbons (1.52 Å). This may be depicted in the language of the resonance theory as follows (see pages 236 and 318):

$$\underset{\text{I}}{CH_2=CH-CH=CH_2} \leftrightarrow \underset{\text{II}}{\overset{+}{C}H_2-CH=CH-\overset{-}{C}H_2} \leftrightarrow$$

$$\leftrightarrow \underset{\text{III}}{\overset{-}{C}H_2-CH=CH-\overset{+}{C}H_2} \leftrightarrow \underset{\text{IV}}{\overset{\uparrow}{C}H_2-CH=CH-\overset{\downarrow}{C}H_2}$$

In formula IV the arrows above the extreme carbon atoms denote lone electrons and their opposite direction signifies an opposite spin and, hence, that these electrons are paired.

The structure of 1,3-butadiene expressed in the language of LCAO was considered on page 322.

And, finally, hydrocarbons such as **divinylmethane** or **diallyl**

$CH_2=CH-CH_2-CH=CH_2$ — Divinylmethane

$CH_2=CH-CH_2-CH_2-CH=CH_2$ — Diallyl

or hydrocarbons with double bonds still more remote from each other have so-called **isolated double bonds** which behave independently of each other.

A. General Methods of Preparation of Dienes

The general methods of preparing dienes are the same as for olefins: the elimination of a halogen atom from the neighbouring carbon atoms by zinc; the elimination of a hydrogen halide by sodium alkoxide, the dehydration of glycols. For one double bond to be formed, one act of elimination is sufficient, but if two double bonds are to be formed two acts are required, which may be different. For example, allene is normally produced by converting glycerol into 1,2,3-tribromopropane and by eliminating first hydrogen bromide from it and then bromine:

$$BrCH_2-CHBr-CH_2Br+CH_3ONa \longrightarrow CH_2=CBr-CH_2Br+CH_3OH+NaBr$$
$$CH_2=CBr-CH_2Br+Zn \longrightarrow CH_2=C=CH_2+ZnBr_2$$

Dienes with isolated double bonds can be obtained in the same way.

Hydrocarbons of the *diallyl* type are easily made also by coupling allyl radicals through the action of a metal on an allyl halide:

$$2CH_2=CH-CH_2Cl+2Na \longrightarrow CH_2=CH-CH_2-CH_2-CH=CH_2+2NaCl$$

or by the action of an allyl halide with its mobile halogen atom on a Grignard reagent which already contains a double bond in the radical:

$$CH_2=CH-CH_2MgBr+ClCH_2-CH=CH_2 \longrightarrow$$
$$\longrightarrow CH_2=CH-CH_2-CH_2-CH=CH_2+MgClBr$$

B. Preparation of 1,3-Dienes

As regards 1,3-dienes which serve as the starting material for the production of synthetic rubber, many special methods have been devised for their preparation. This is especially true of the first two members of the homologous series of hydrocarbons with conjugated double bonds—1,3-butadiene and 2-methyl-1,3-butadiene (isoprene).

1,3-*Butadiene* can be synthesized by means of the following methods.

1. The aldol prepared by the aldol condensation of acetaldehyde is reduced to 1,3-glycol:

$$CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-\underset{\underset{O}{||}}{C}-H \xrightarrow{2H} CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-\underset{\underset{OH}{|}}{CH_2}$$

which is then dehydrated into butadiene by the action of acid or catalytically—in the presence of Al_2O_3:

$$CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-\underset{\underset{OH}{|}}{CH_2} \xrightarrow[-2H_2O]{} CH_2=CH-CH=CH_2$$

This synthesis proves the normal structure of the chain and the presence of two double bonds. The 1,3-position of double bonds is conclusively confirmed by the reactions typical of conjugated diene bonds (see below).

2. The industrial synthesis of 1,3-butadiene (also referred to simply as butadiene) by the Lebedev method, which has been in use in the USSR since 1932, boils down, in the long run, to the following. Ethanol is passed at 400-500°C over a catalyst consisting of the oxides MgO and ZnO. This catalyst is capable of dehydrogenating alcohols into aldehydes, and being alkaline, can cause the aldol condensation of the aldehyde. Dehydrogenation and hydrogenation, one being the converse of the other, are catalysed by the same catalysts; therefore, the same catalyst is employed to effect the addition of the hydrogen, which has been evolved in the dehydrogenation of the alcohol, to the aldehyde group. And, finally, this catalyst also brings about (like alumina) dehydration. Thus, the manifold action of the Lebedev catalyst makes it possible to convert the alcohol into butadiene in excellent yield by a single run of the alcohol vapour over the catalyst:

$$C_2H_5OH \xrightarrow[-H_2]{} CH_3-C\overset{H}{\diagdown\!\!\diagup}O$$

$$2CH_3-C\overset{H}{\diagdown\!\!\diagup}O \longrightarrow \underset{\text{Aldol}}{CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-C\overset{H}{\diagdown\!\!\diagup}O} \xrightarrow[-H_2O]{} \underset{\text{Crotonaldehyde}}{CH_3-CH=CH-C\overset{H}{\diagdown\!\!\diagup}O}$$

$$CH_3-CH=CH-C\overset{H}{\diagdown\!\!\diagup}O \xrightarrow{+H_2} CH_3-CH=CH-CH_2OH$$

$$CH_3-CH=CH-CH_2OH \xrightarrow[-H_2O]{} CH_2=CH-CH=CH_2$$

The last stage of the reaction consists of the dehydration and isomerization (migration of the double bond).

The summary equation of the process is:

$$2C_2H_5OH \longrightarrow C_4H_6+2H_2O+H_2$$

3. The method developed by Reppe is based on the condensation of acetylene with formaldehyde, followed by hydrogenation of the resulting butanediol into 1,4-butanediol, partial dehydration of

this diol and phosphoric acid to tetrahydrofuran and complete dehydration of the last compound over $NaPO_3$ to 1,3-butadiene:

$$2CH_2O + HC \equiv CH \longrightarrow HOCH_2-C \equiv C-CH_2OH$$

$$HOCH_2-C \equiv C-CH_2OH \xrightarrow{H_2/Ni} HOCH_2-CH_2-CH_2-CH_2OH$$

$$HOCH_2-CH_2-CH_2-CH_2OH \xrightarrow[-H_2O]{H_3PO_4} \begin{matrix} H_2C-CH_2 \\ | \quad | \\ H_2C \quad CH_2 \\ \diagdown \quad \diagup \\ O \end{matrix}$$

$$\begin{matrix} H_2C-CH_2 \\ | \quad | \\ H_2C \quad CH_2 \\ \diagdown \quad \diagup \\ O \end{matrix} \xrightarrow[-H_2O]{NaPO_3} CH_2=CH-CH=CH_2$$

4. The two-stage dehydrogenation of butane first to butylene (the catalyst used is chromium oxide on alumina) and then to butadiene over ferric oxide on alumina (A. A. Balandin and O. K. Bogdanova):

$$CH_3-CH_2-CH_2-CH_3 \xrightarrow{\text{catalyst}} CH_3-CH_2-CH=CH_2+H_2$$

$$CH_3-CH_2-CH=CH_2 \xrightarrow{\text{catalyst}} CH_2=CH-CH=CH_2+H_2$$

The process can be accomplished on an industrial scale in one stage as well.

5. The condensation of propylene with formaldehyde over an acid catalyst (the Prins reaction; see page 342):

$$H-C(=O)-H \xrightarrow{H^+} H-C^+(-OH)-H$$

$$CH_3-CH=CH_2 + CH_2(+H_2O+HO) \xrightarrow{-H^+} CH_3-CH(HO)-CH_2-CH_2-HO \xrightarrow[-H_2O]{+CH_2O}$$

$$\longrightarrow CH_3-HC\begin{matrix} CH_2-CH_2 \\ \diagdown \quad \diagup \\ O \quad O \\ \diagup \quad \diagdown \\ CH_2 \end{matrix}$$

Formaldehyde and water are split off from the resulting homologue of 1,3-dioxan, which gives butadiene as a result:

$$CH_3-HC\begin{matrix} CH_2-CH_2 \\ \diagdown \quad \diagup \\ O \quad O \\ \diagup \quad \diagdown \\ CH_2 \end{matrix} \xrightarrow{-H_2O;\ -CH_2O} CH_2=CH-CH=CH_2$$

This method is undoubtedly very promising.

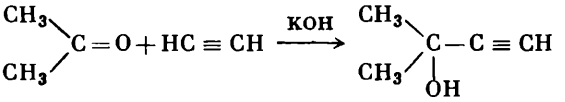
6. Partial hydrogenation of vinylacetylene (page 355):

$$CH_2=CH-C\equiv CH \xrightarrow{H_2(catalyst)} CH_2=CH-CH=CH_2$$

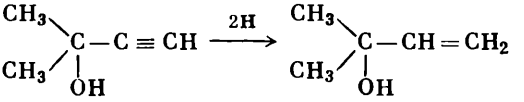
is also used in some countries for the production of butadiene.

The nearest homologue of butadiene is **isoprene**, which has become very important in the recent years. It can be made by methods only partly similar to the syntheses of butadiene.

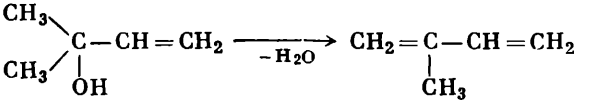
1. The Favorsky condensation of acetone with acetylene (KOH being used as catalyst) gives *dimethylethynylcarbinol*



which is hydrated (electrochemically) to *dimethylvinylcarbinol*



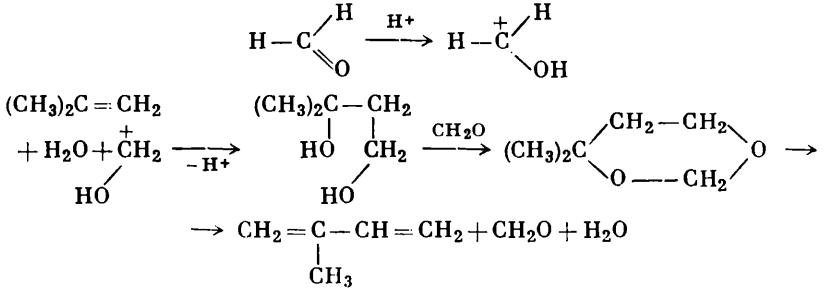
the latter being dehydrated to isoprene:



2. Dehydrogenation of isoamylene over an alumina-chromium oxide catalyst:

$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH=CH_2 \xrightarrow{Al_2O_3;\ Cr_2O_3;\ Cu^{2+}} CH_2=\underset{\displaystyle CH_3}{\underset{|}{C}}-CH=CH_2+H_2$$

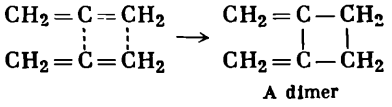
3. The condensation of isobutylene with formaldehyde gives a homologue of 1,3-dioxan, which is dehydrated to isoprene:



All these reactions provide a good evidence of the structure of isoprene as 2-methyl-1,3-butadiene.

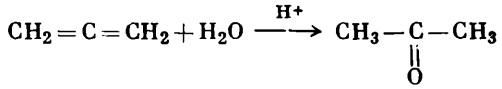
C. Reactions of Dienes

The reactions of allenes do not differ to any appreciable degree from those of olefins, except for the polymerization on heating up to 150°C. In this reaction, allene forms dimers, trimers and tetramers with four-membered rings (S. V. Lebedev):



A dimer

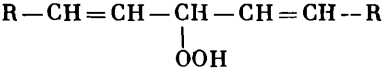
On hydration in acid medium allene gives acetone:



The reactions of dienes with isolated double bonds do not differ from the behaviour of olefins either: the addition occurs at both double bonds, and with a deficiency of the reagent only one bond is first involved.

Only the specific properties of the methylene group in **divinylmethane** and its derivatives ought to be mentioned. The enhanced ability of the hydrogens of the methyl or methylene group contiguous to the double bond to be abstracted as protons has already been pointed out (page 344). For example, the methyl group in propylene can be subjected under drastic conditions (L'vov) to metaleptic substitution by chlorine with the formation of allyl chloride. In compounds with the bond systems

the hydrogen of the methylene group becomes even more mobile. Such dienes are especially capable of being oxidized by atmospheric oxygen with the formation of hydroperoxides (page 259):



The reactions of 1,3-dienes *with conjugated double bonds* differ most strongly from the reactions of olefins and are of the greatest importance.

The conjugation of double bonds (page 362) manifests itself energetically in a somewhat lower energy (by a factor of 3-5 kcal/mole) of the system and, consequently, in a somewhat lower reactivity of the carbon atoms 2 and 3, while the carbons 1 and 4 have a normal or even increased tendency to add both electrophilic and radical reagents.

Dienes with conjugated double bonds are characterized by the following reactions.

1. Nascent hydrogen (*radical attack*) adds on to such dienes in the following way:

$$CH_2=CH-CH=CH_2 \xrightarrow{+2H} CH_3-CH=CH-CH_3$$

and gaseous hydrogen over nickel or platinum hydrates all the four carbons, giving rise to butane.

2. Bromine and chlorine (*electrophilic attack*) add on to the dienes largely at the 1,4-positions:

$$CH_2=CH-CH=CH_2 \xrightarrow{+Br_2} \underset{\displaystyle Br}{\overset{\displaystyle |}{CH_2}}-CH=CH-\underset{\displaystyle Br}{\overset{\displaystyle |}{CH_2}}$$

but simultaneously a 1,2-addition product is also formed:

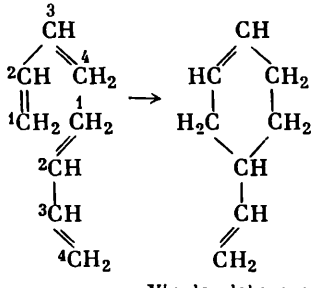
$$\underset{\displaystyle Br}{\overset{\displaystyle |}{CH_2}}-\underset{\displaystyle Br}{\overset{\displaystyle |}{CH}}-CH=CH_2$$

3. Hydrogen chloride adds on by four-fifth of its amount at the 1,4-positions and only by one-fifth at the 1,2-positions:

$$CH_2=CH-CH=CH_2 \xrightarrow{+HCl} CH_3-CH=CH-CH_2Cl$$

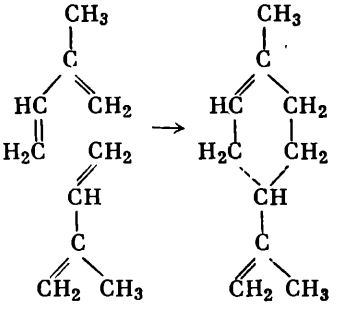
The mechanism of addition of hydrogen bromide is less clear since the corresponding bromides readily undergo **allylic rearrangement** (see Volume IV) with the migration of the double bond, and it is not easy to decide whether the predominantly formed $CH_3-CH=CH-CH_2Br$ is the product of the allylic rearrangement of the original 1,2-addition product. Extensive studies that have contributed to the solution of the problems associated with 1,2- and 1,4-additions to dienes are due to A. A. Petrov.

4. An important 1,4-addition reaction is the Lebedev dimerization of butadiene on heating up to about 150°C into **vinylcyclohexene**:



Vinylcyclohexene

Isoprene under these conditions forms **dipentene**



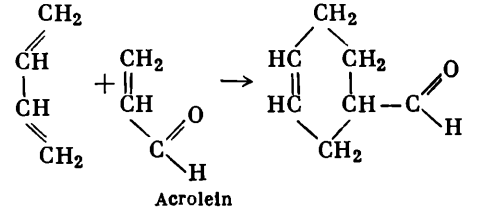
Dipentene

which is found in the resin of coniferous plants in the form of the so-called limonene (Vol. II) and is in fact a terpene—a constituent of turpentine.

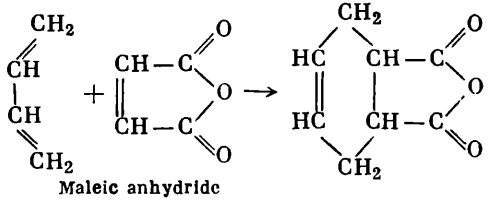
In these reactions one molecule of a diene reacts at the 1,4-positions, adding on to the second molecule of the diene at the 1,2-positions.

The Lebedev dimerization turned out to be a particular case of the subsequently discovered **diene synthesis** or the **Diels-Alder reaction** (1928)* which has become one of the most prolific and versatile reactions at the disposal of the organic chemist.

5. The Diels-Alder reaction. Dienes add at the 1,4-positions the derivatives of alkenes, which are called **dienophiles** (the addition takes place at the *cis*-position):



Acrolein



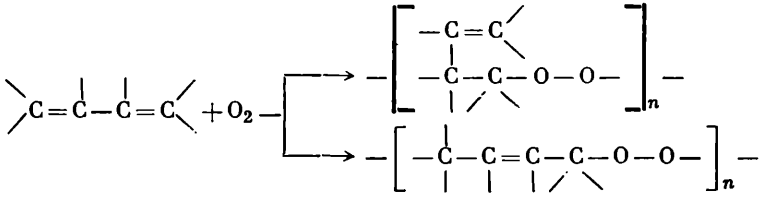
Maleic anhydride

The dienophiles in these examples are acrolein, which is the simplest unsaturated aldehyde, and the anhydride of maleic acid. Addi-

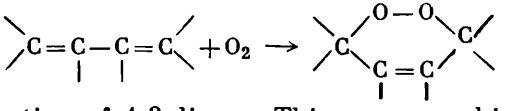
* An intensive study of the reaction by Diels and Alder earned them the Nobel Prize in chemistry in 1950.— *Tr.*

tion of such active dienophiles occurs at room temperature or on gentle heating. Active dienophiles are substances containing systems of C=C—C=O bonds which are also conjugated. In the subsequent years the number of dienophiles kept on increasing; unsymmetrically built halogen derivatives such as $CH_2=CH—Cl$ and $CH_2=CH—CCl_3$, and vinyl esters of the general formula $CH_2=CH—OR$ proved to be good dienophiles. Even unsymmetrical hydrocarbons of the general formula $CH_2=CH—R$ were introduced into diene synthesis, which has become a universal method of building six-membered rings.

6. The reaction of 1,3-dienes with molecular oxygen may proceed with the formation of both polymeric (low-molecular-weight) peroxides—the 1,2- and 1,4-addition products



and peroxide compounds such as the adducts of diene synthesis:



7. Polymerization of 1,3-dienes. This process, which is of great industrial interest, may occur, in the presence of a number of reagents, either entirely by the 1,4-addition mechanism (under the action of lithium alkyls) or by a mixed 1,2- and 1,4-addition mechanism under the influence of chain-reaction initiators (compounds which generate free radicals, say, peroxides, diazoamino compounds) and also of metallic sodium. Organometallic polymerization initiators of the RLi type cause anionic polymerization which begins with a nucleophilic attack on a diene by the alkyl anion R^-. We shall give the summary equations of the anionic 1,4-polymerization of butadiene

$$n CH_2=CH-CH=CH_2 \xrightarrow{C_4H_9Li}$$

$$\longrightarrow C_4H_9-(CH_2-CH=CH-CH_2)_{n-1}-CH_2-CH=CH-\bar{C}H_2+Li^+$$

and isoprene

$$n CH_2=\underset{\displaystyle CH_3}{\underset{|}{C}}-CH=CH_2 \xrightarrow{C_4H_9Li}$$

$$\longrightarrow C_4H_9-(CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH-CH_2)_{n-1}-CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH-\bar{C}H_2+Li^+$$

It has been found later that natural rubber is identical with the product of the anionic 1,4-polymerization of isoprene and also has the *cis*-configuration (page 380).

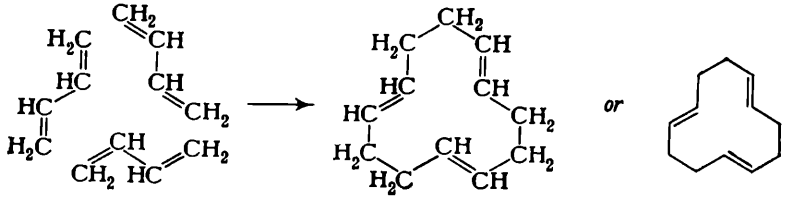
The schematic equation of the radical 1,2-1,4 polymerization of butadiene is as follows:

$$n CH_2=CH-CH=CH_2 \xrightarrow{R\cdot}$$

$$\rightarrow R-CH_2-CH=CH-CH_2-CH_2-\underset{\underset{\|}{CH_2}}{\overset{|}{CH}}-CH_2-\underset{\underset{\|}{CH_2}}{\overset{|}{CH}}-CH_2-CH=CHCH_2- \ldots$$

The Lebedev synthetic butadiene rubber belongs to this type of polymers.

8. Under the influence of Ziegler catalyst [$TiCl_4 + Al(C_2H_5)_3$] butadiene trimerizes into a twelve-membered ring—cyclododecatriene:



This trimerization also takes place at the 1,4-positions.

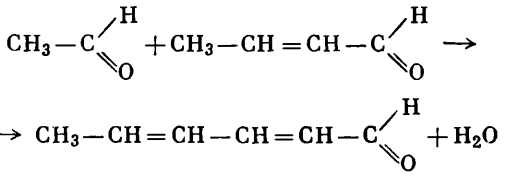
All that has been said above provides an idea of the 1,4-addition reactions as the most characteristic feature of the chemistry of conjugated systems with two double bonds or, as they are conveniently termed, π,π-conjugated systems. Other types of conjugation, which are also characterized by 1,4-additions, will be encountered later on.

3.4. Polyenes

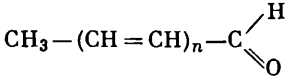
The systematic synthesis of polyenes with a normal chain and with conjugated double bonds only was accomplished by means of the croton condensation of acetaldehyde (R. Kuhn).

The point is that crotonaldehyde is capable, owing to the mobility of the hydrogen atoms of its methyl group, of entering into a conden-

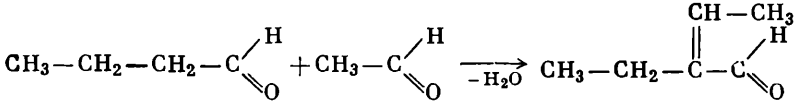
sation reaction with acetaldehyde, thereby lengthening its system of conjugated double bonds (croton condensation):



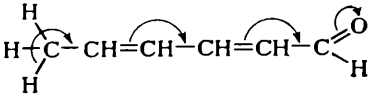
The resulting new aldehyde—2,4-hexadienal—reacts with a new molecule of acetaldehyde, the reaction being of the same type of condensation, etc., so that an ordinary croton condensation gives, as by-products, a series of unsaturated aldehydes of the general formula



It should be stressed that saturated aldehydes enter into condensation reactions only at the α-linkage, for example,



The next CH_2 linkages (β-, γ-, etc.) and the CH_3 group exhibit a hydrocarbon character and the hydrogen atoms in them are fixed (inactive). But the system of conjugated double bonds is "electroconductive" and transmits completely the effect of the carbonyl to the last methyl group, rendering its hydrogen atoms active. This behaviour is typical of a chain of conjugated double bonds. Instead of the inductive effect ($-I$ effect in the example given above) which is rapidly suppressed along the saturated chain, there is operating a $-T$ effect (the conjugation effect, or $-C$ effect)* which is suppressed but to a very slight degree and is well transmitted:



* As has already been pointed out (page 239), the *T* effect differs from the *M* effect of the same direction (i.e., of the same sign) in that it reveals itself only in reactions and not in the non-reacting molecule. The conjugation effect is a combination of these two effects.

If an unsaturated aldehyde is acted on by ethylmagnesium bromide, a corresponding alcohol is obtained, which is dehydrated to a polyene:

$$CH_3-(CH=CH)_n-\underset{\underset{O}{\|}}{C}-H+C_2H_5MgBr \longrightarrow$$

$$\longrightarrow CH_3-(CH=CH)_n-\underset{\underset{OH}{|}}{CH}-CH_2-CH_3 \xrightarrow[-H_2O]{}$$

$$\longrightarrow CH_3-(CH=CH)_n-CH=CH-CH_3$$

Alkylpolyenes (up to C_{10}) are colourless, though 2,4,6,8,10,12-tetradecahexaene is a bright-yellow compound, which is too high-melting for a hydrocarbon (m.p. 205°C). At present high-molecular-weight compounds are also known, which contain only conjugated double bonds ...—CH=CH—(CH=CH)$_n$—.... These are solid thermally stable black-coloured compounds exhibiting semiconducting properties. They are prepared, for example, by dehydration of polyvinyl alcohol:

$$\ldots-\underset{\underset{OH}{|}}{CH}-CH_2-\underset{\underset{OH}{|}}{(CH}-CH_2)_n-\ldots$$

Some of the lower polyenes having an isoprenoid skeleton occur in nature. Such are the aliphatic terpenes of the composition $C_{10}H_{16}$, which are found in certain ethereal oils (e.g., hop oil). They include **myrcene**

$$CH_3-\underset{\underset{CH_3}{|}}{C}=CH-CH_2-CH_2-\underset{\underset{CH_2}{\|}}{C}-CH=CH_2$$

and **ocimene**

$$CH_3-\underset{\underset{CH_3}{|}}{C}=CH-CH_2-CH=\underset{\underset{CH_3}{|}}{C}-CH=CH_2$$

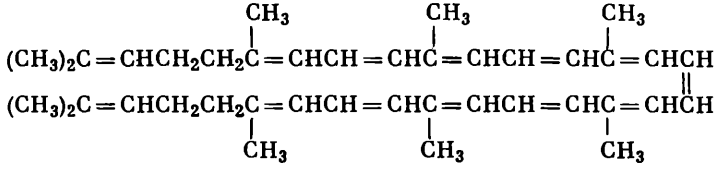
The structure of these compounds has been established by means of ozonization.

An interesting hydrocarbon has been detected in the shark liver oil. This is **squalene**, $C_{30}H_{50}$, which may be regarded as being built up of two fragments of natural isoprene rubber (three units in each) joined in a "head-on" manner, and with two hydrogen atoms at the ends:

$$(CH_3)_2C=CHCH_2CH_2\underset{\underset{CH_3}{|}}{C}=CHCH_2CH_2\underset{\underset{CH_3}{|}}{C}=CHCH_2$$

$$(CH_3)_2C=CHCH_2CH_2\underset{\underset{CH_3}{|}}{C}=CHCH_2CH_2\underset{\underset{CH_3}{|}}{C}=CHCH_2$$

The red colour of ripe tomatoes is due to the presence of the hydrocarbon **lycopene**, $C_{40}H_{56}$, which has a long system of conjugated bonds in its polyisoprenoid molecule:

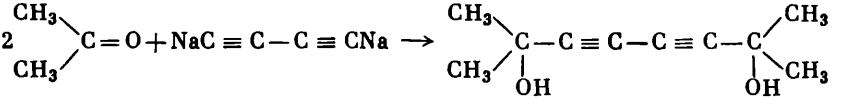


Lycopene is isomeric with **carotenes**, the orange pigments of carrots, whose formulas include one or two six-membered rings and have therefore one or two double bonds less than lycopene.

These isoprenoid compounds will be discussed in more detail in Volume IV.

A. Cumulenes

Cumulenes were first prepared by R. Kuhn. These are polyenes with cumulated double bonds only. The reaction carried out by Kuhn proceeds via glycols as follows:



Then he reduced this type of glycol, by means of $CrCl_2$ to cumulenes

$$(CH_3)_2C=C=C=C=C=C(CH_3)_2$$

3.5. Enynes

These are the simplest unsaturated hydrocarbons containing double bonds and one triple bond. They were mentioned in passing on page 355.

Vinylacetylene or **butenyne**, a representative of this series, is made by dimerization of acetylene in a solution of CuCl and NH_3 + + NH_4Cl (Nieuwland):

$$2CH\equiv CH \longrightarrow CH_2=CH-C\equiv CH$$

The by-product formed in this process is a trimer of acetylene—**divinylacetylene**, $CH_2=CH-C\equiv C-CH=CH_2$.

Divinylacetylene, which is an isomer of benzene, is explosive, unstable and has a tendency to polymerize spontaneously.

Vinylacetylene is converted by hydrochlorination into chloroprene:

$$CH_2=CH-C\equiv CH+HCl \longrightarrow CH_2=CH-\underset{\displaystyle Cl}{\underset{|}{C}}=CH_2$$

from which synthetic chloroprene rubber is then produced.

The presence in the vinylacetylene molecule of a mobile (active) acetylenic hydrogen atom is also responsible for the occurrence of all the reactions characteristic of the compound: replacement by Ag, Cu^I, MgCl (under the action of a Grignard reagent). With ketones in the presence of KOH, vinylacetylene reacts by the Favorsky mechanism to form vinylethynyldiallylcarbinols (I. N. Nazarov):

$$CH_2=CH-C\equiv CH+CH_3-\underset{\displaystyle O}{\underset{\|}{C}}-CH_3 \xrightarrow{KOH} CH_2=CH-C\equiv C-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-OH$$

which are capable of various conversions and have therefore found wide application in synthesis.

A. A. Petrov, who studied the reactions of addition to enynes with a conjugated system of C=C—C≡C bonds and isolated C=C and C≡C bonds, formulated the following regularities.

In unconjugated enynes, the halogenation proceeds in the first place at a double bond, and the addition of hydrogen halides first at the triple bond.

Enynes with conjugated bonds are hydrogenated (catalytically or electrochemically) first across the triple bond. Vinylacetylene and its homologues of the structure RCH=CH—C≡CH add bromine chiefly at the 1,4-positions, forming an allenic system of π-bonds:

$$CH_2=CH-C\equiv CH+Br_2 \longrightarrow BrCH_2-CH=C=CHBr$$

The homologues of vinylacetylene of the type CH_2=CH—C≡CR are brominated and chlorinated at the double bond, and the iodination proceeds at the triple bond. Hydrogen halides also attack the triple bond but partly add on at the 1,4-positions.

The triple bond has a stronger tendency towards 1,3-dipolar additions (see "Heterocyclic Compounds", Volume III) of diazomethane, etc.

3.6. Polyynes

The simplest polyyne—**diacetylene**, or **butadiyne**, HC≡C—C≡CH, is most simply prepared from butynediol (page 359):

$$HOCH_2-C\equiv C-CH_2OH \xrightarrow{SOCl_2} ClCH_2-C\equiv C-CH_2Cl \xrightarrow{NaOC_2H_5} HC\equiv C-C\equiv CH$$

Diacetylene is a colourless liquid with b.p. 10°C, which is extremely unstable and liable to polymerization. Both its hydrogens are replaced by metals and various syntheses can be accomplished via its sodium or magnesium derivative (page 358).

Diacetylene and formaldehyde can be used to prepare a diol by the Reppe reaction:

$$HOCH_2-C\equiv C-C\equiv C-CH_2OH$$

and then the hydroxyls in the diol are replaced by chlorine and HCl is eliminated by the action of ammoniacal silver oxide, as a result of which a silver derivative of triacetylene (hexatriyne) is directly obtained:

$$HC\equiv C-C\equiv C-C\equiv CH$$

This hydrocarbon polymerizes spontaneously even at —20°C.

When the copper salts of acetylenes of the type $R-C\equiv CH$ and of polyynes of the type $R-(C\equiv C)_n-H$ are oxidized by atmospheric oxygen or by $K_3Fe(CN)_6$, the residues of their molecules are coupled and polyynes are obtained:

$$2R-(C\equiv C)_n-Cu+O_2 \longrightarrow R-(C\equiv C-C\equiv C)_n-R+2CuO$$

In this way, V. V. Korshak and A. M. Sladkov prepared, from diacetylene, a black-coloured mixture of insoluble polymer homologues:

$$\ldots-C\equiv C-C\equiv C-C\equiv C-C\equiv C-\ldots$$

In fact, this is a new allotropic modification of carbon.

Quite unexpected was the discovery of polyyne hydrocarbons and also of the corresponding alcohols and esters in certain mushrooms (E.P.G. Jones). For example, the following polyynes were discovered:

$$CH_3-(C\equiv C)_5-CH=CH_2 \quad \text{and} \quad CH_3-CH=CH-(C\equiv C)_4-CH=CH_2$$

3.7. Rubbers

Natural rubber (caoutchouc) is produced from a milky fluid known as **latex** which is found in many plants. The main source of natural rubber is the tree *Hevea braziliensis*, native to Brazil but now grown extensively also in cultivated plantations in southern Asia (Indone-

sia). The ordinary fig (*Ficus*) and certain plants of the Compositae (dandelion) family (Kok-Saghyz, Tau-Saghyz) also contain the latex.

Natural rubber was brought to Europe only at the beginning of the eighteenth century. The American Indians—the discoverers of natural rubber—made use of crude rubber, covering clay forms with several layers of latex and drying them. The elastic and waterproof layer formed was then separated from the clay by crushing the form and removing its fragments through the opening of the resulting vessel. The rubber articles thus produced were utilized as flasks.

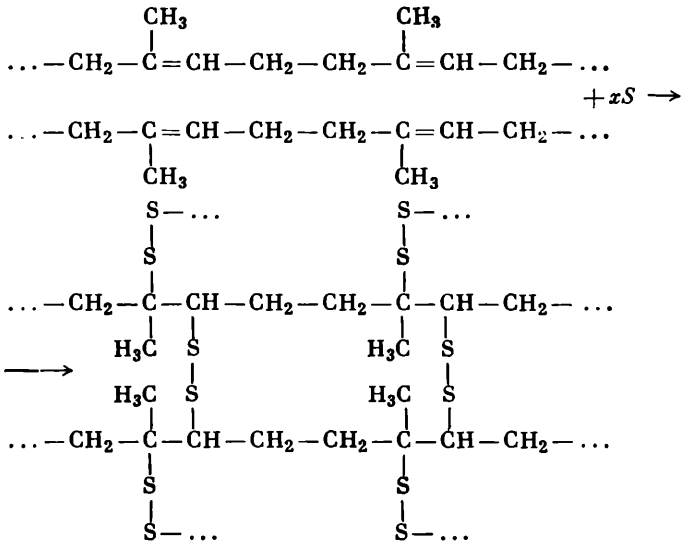
In England, chemists have learned to dissolve such crude rubber in the hydrocarbons of coal tar (a mixture of benzene and its homologues) and produce in this way a rubber glue. The first application of such solutions was in the impregnation of fabrics to render them waterproof. For the fabric not to be sticky on one side it was folded in half. Such a waterproof material is known by the name of its original manufacturer, Charles Macintosh. Raincoats made of such a waterproof material were given the same name. Further attempts to eliminate the tackiness of the fabric by adding special powders, including flowers of sulphur, led to the discovery of **vulcanization**—the conversion of crude rubber into synthetic rubber.

Natural rubber is produced and processed as follows.

The milky fluid or latex collected by "tapping" the bark of the tree (a small incision is made and the latex is allowed to ooze out) is coagulated by addition of acetic acid. The settled elastic lumps of crude rubber are separated (lifted from the vat) and rolled into sheets by passing the mass repeatedly between serrated rollers. In the course of rolling the highly elastic crude rubber is converted into a plastic material which can be mixed with powdered fillers, in particular with sulphur for vulcanization (curing), with accelerators to expedite the reaction of rubber with sulphur, and with fillers such as carbon black (grey rubbers), silicon oxide (white rubbers), sulphurous antimony (red rubbers).

The rolling process, as was found out one hundred years later after its introduction, involves a very interesting mechanical-chemical process. Crude rubber is a mixture of molecules of the composition $(C_5H_8)_n$ with a molecular weight of 100,000-150,000. Rubber molecules having an enormous length are broken homolytically under the mechanical influence of rollers and the newly formed ends with unpaired electrons (free-radicals ends) absorb the oxygen of the air, forming peroxides at the ends of still long molecules which are then stabilized, giving up the peroxide oxygen for oxidation. With decreasing length of the molecules the plasticity of rubber increases and it becomes possible to introduce sulphur and fillers. Filled rubber is shaped into articles (e.g., tyres) which are vulcanized on heating. In the vulcanization process, sulphur adds at the unsaturated bonds, forming "bridges" and "cross-linking" the linear molecules into prac-

tically infinite three-dimensional or network structures:

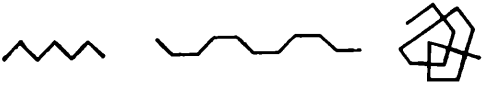


After the molecular chains are cross-linked the rubber loses plasticity and acquires elastic properties.

The vulcanized filled rubber is called an *elastomer*.

If the disulphide bridges are sparse, the network system retains mobility and, hence, elasticity. If there are many disulphide bridges, the system becomes rigid (ebonite). Apart from sulphur, there are other vulcanizing agents which act by way of cross-linking the molecules.

What is responsible for the elasticity of natural rubber and other high-molecular-weight compounds with very long linear molecules? A chain of saturated carbon atoms with valence angles of 109° may assume the various conformations as a result of free rotation about the C—C bonds. For example,



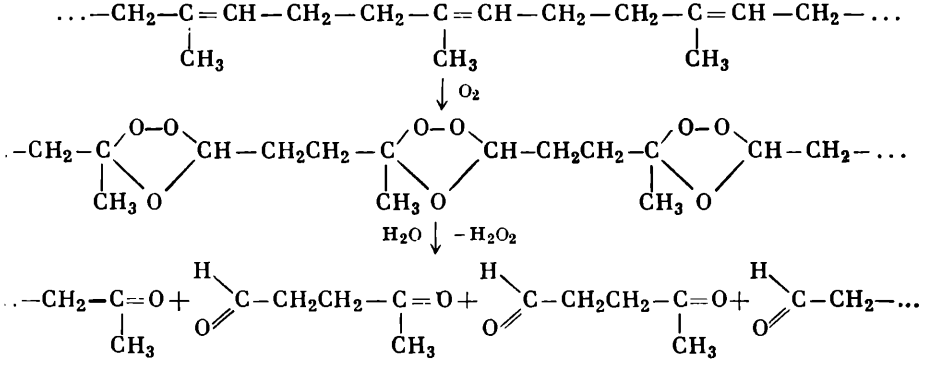
The double bonds in the molecule of natural rubber occupying the 1,5-positions do not alter the situation significantly.

If the molecule is enormously long, the most probable is the randomly (chaotically) twisted conformation of the elastomer molecule When a piece of natural rubber is stretched, the thread-like molecules are partly straightened out, but a less regular arrangement of

the molecules is more probable, and when the tensile load is removed they again coil up. This is easily understood if we replace mentally the carbon atoms of a stretched molecule (a filament of rubber) with the molecules of any gas arranged in a row. The random thermal motion of the gas molecules will destroy the row and scatter the molecules in different directions. Let us now suppose that the molecules are joined together in such a manner that each molecule is at a strictly definite distance from its two neighbours, that is, they are united into a chain by valences. Then the random thermal motion will reduce the chain size and thus act in a direction opposite to stretching.

Structure of Natural Rubber (Caoutchouc). When subjected to pyrolysis natural rubber depolymerizes with the formation of isoprene. The olefinic bonds contained in the rubber molecule may be hydrogenated catalytically, one C_5H_8 unit consuming two hydrogen atoms. Rubber adds bromine and hydrogen bromide also at the unsaturated bonds.

The ozonolysis of rubber (Harries) results in the formation of levulinic aldehyde, the only product of the reaction. The reaction may be schematically depicted as follows:



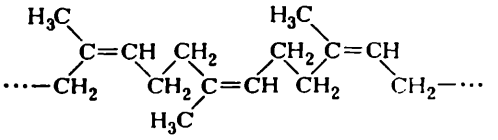
Thus, the ozonolysis reveals the presence of a repeating fragment in the structure of the rubber macromolecule.

Determination of the viscosity of rubber solutions allows one to deduce the average molecular weight of rubber. All that has been said leads to the formula of natural rubber given above (Staudinger).

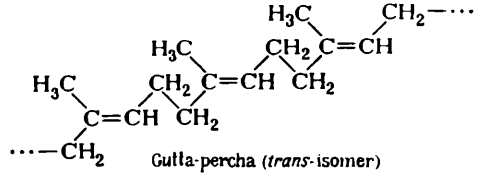
A natural product similar to rubber, **gutta-percha**, is very rigid at ordinary temperature and only at elevated temperature (70-100°C) does it become plastic.

Gutta-percha is produced from the plants growing in Indonesia; it is also contained in the spindle tree (*Euonymus*) which grows in the USSR. Gutta-percha is used in the cable industry. Its composition, chemical properties and ozonolysis products do not differ from those

of rubber, which means that their structures are the same. As shown by X-ray diffraction studies, these materials differ from each other stereochemically: rubber is composed of long chains built up of isoprene units arranged in the *cis*-form, whereas gutta-percha is the *trans*-form*:



Rubber (*cis*-isomer)

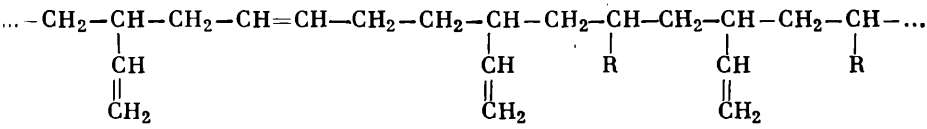


Gutta-percha (*trans*-isomer)

Synthetic Rubbers. The first commercial synthetic rubber was butadiene rubber (S. V. Lebedev) produced from butadiene by polymerization with metallic sodium (sodium-butadiene rubber). Later a more convenient method of polymerization was devised, in which butadiene is emulsified in water by adding soaps (page 221). The polymerization of drops of butadiene is caused by addition of an initiator which generates free radicals (e.g., diazoaminobenzene, see Volume III). The structure of butadiene rubber as a product of mixed 1,2 and 1,4 polymerization has already been described (page 370). Just as in the case of natural rubber, butadiene rubber is processed into an elastomer. To vary the properties of rubber, butadiene is often copolymerized with other unsaturated compounds such as styrene, $C_6H_5-CH=CH_2$, acrylonitrile, $CH_2=CH-C\equiv N$ (page 409), etc. This copolymerization leads to the formation of polybutadiene macromolecules with the residues of the comonomer molecules incorporated into them. Styrene-butadiene rubber (SBR) is abrasive resistant and is used for the production of tyres; butadiene-acrylonitrile rubbers (nitrile rubbers) are noted for their excellent resistance to hydrocarbons (gasoline or petrol) and are utilized for manufacturing gasoline pipes, hoses, etc. Their structure may be schema-

* The *cis-trans* isomerism is discussed on page 424.

tically depicted thus:



where $R = C_6H_5$ or $C \equiv N$.

The copolymerization of isobutylene with a small amount of butadiene gives butyl rubber which is chemically more stable (it contains less double bonds) but capable of being vulcanized due to the presence of unsaturated butadiene units.

An analogue of isoprene is chloroprene (2-chloro-1,3-butadiene) which is readily polymerized into petrol-resistant chloroprene rubber.

3.8. Unsaturated Halogen Derivatives

We have already met with many unsaturated halogen derivatives and with some of the methods of their synthesis. The formulas, names and physical properties of a number of unsaturated halogen derivatives are given in Table 3.4. At this point it is necessary to remind the reader briefly of the methods of synthesis of these halogen derivatives and to compare them.

The simplest halogen derivative of ethylene is a vinyl halide. From the practical point of view, a very important halide is vinyl chloride, $CH_2=CHCl$, which is utilized in enormous quantities for polymerization into polyvinyl chloride. It is produced by the following industrial methods.

1. The cracking of dichloroethane (Al_2O_3 being used as catalyst):

$$ClCH_2-CH_2Cl \longrightarrow CH_2=CHCl + HCl$$

2. The addition of hydrogen chloride to acetylene.

This method is employed in countries where no sufficient petroleum is available and, hence, there is a deficiency of ethylene:

$$HC \equiv CH + HCl \xrightarrow{AlCl_3} CH_2=CHCl$$

These two methods can be combined by making use of the hydrogen chloride evolved in the cracking of dichloroethane for hydrochlorination.

Vinylidene chloride, $CH_2=CCl_2$, which is utilized, like vinyl chloride, for polymerization, is obtained through the removal of HCl by alkali from trichloroethane which in its turn is formed by addition of chlorine to vinyl chloride:

$$CH_2=CHCl + Cl_2 \longrightarrow CH_2Cl-CHCl_2 \xrightarrow[-HCl]{} CH_2=CCl_2$$

TABLE 3.4. **Unsaturated Halogen Derivatives**

Formula	Name		m.p., °C	b.p., °C	Density, d_4^{20}	Refractive index n_D^{20}
	trivial	Geneva				
$CH_2=CHCl$	Vinyl chloride	Chloroethene	−159.7	−13.9	0.919 (d_4^{15})	—
$CH_2=CHBr$	Vinyl bromide	Bromoethene	−137.8	+15.8	1.517 (at 14°C)	1.4462
$CH_2=CHI$	Vinyl iodide	Iodoethene	—	56.5	2.0370	—
$CH_3-CH=CHCl$	Propenyl chloride	1-Chloro-1-propene (*cis*-)	−134.8	37.4	0.935 (d_{25}^{15})	—
$CH_3-CCl=CH_2$	Isopropenyl chloride	2-Chloro-1-propene	−137.4	23 (738 mm Hg)	0.918 (at 9°C)	—
$CH_2Cl-CH=CH_2$	Allyl chloride	3-Chloro-1-propene	−136.4	44.6	0.938	1.4154
$CH_2Br-CH=CH_2$	Allyl bromide	3-Bromo-1-propene	−119.4	71.3	1.398	1.4654
$CH_2I-CH=CH_2$	Allyl iodide	3-Iodo-1-propene	−99.3	103.1	1.848 (d_{12}^{12})	—
$CHCl=CHCl$	Dichloroethylene	1,2-Dichloroethene				
	cis-	*cis*-	−80.5	60.8	1.291 (d_4^{15})	1.4519 (at 15°C)
	trans-	*trans*-	−50	48.4	1.265 (d_4^{15})	1.4490 (at 15°C)
$CH_2=CCl_2$	Vinylidene chloride	1,1-Dichloroethene	−122.5	31.7	1.250 (d_4^{15})	—
$CHCl=CCl_2$	Trichloroethylene	Trichloroethene	−73	87.0	1.456 (d_4^{25})	1.4777
$CCl_2=CCl_2$	Tetrachloroethylene	Tetrachloroethene	−22.2	121.0	1.623 (d_4^{15})	1.5053
$CF_2=CF_2$	Tetrafluoroethylene	Tetrafluoroethene	−142.5	−78.4	—	—
$CH\equiv CCl$	Monochloroacetylene	Chloroethyne	—	−32(expl.)	—	—
$CH\equiv CBr$	Monobromoacetylene	Bromoethyne	—	−2	—	—
$CHBr=CHBr$	Dibromoethylene	1,2-Dibromoethene				
	cis-	*cis*-	−53	112.5	2.2846 ($d_4^{17.5}$)	1.5428
	trans-	*trans*-	−6.5	108	2.2667 ($d_4^{17.5}$)	—

The elimination of a hydrogen halide from unsymmetrical halides occurs in accordance with the **Zaitsev rule**: the hydrogen ion is split off from the carbon atom carrying the larger number of halogen atoms (for more detail concerning the Zaitsev rule, see Volume IV, "Elimination Reactions").

Symmetrical dichloroethylene, an isomer of ethylidene chloride, is synthesized by addition of an insufficient amount of chlorine to acetylene; a *trans*-isomer is obtained as a result (*trans*-addition):

$$CH \equiv CH + Cl_2 \longrightarrow CHCl = CHCl$$

Trichloroethylene (*trichloroethene*), $CHCl=CCl_2$, is made by eliminating HCl from tetrachloroethane (the latter is obtained by addition of 2 moles of chlorine to acetylene):

$$Cl_2CH-CHCl_2 \xrightarrow[-HCl]{} CHCl=CCl_2$$

Trichloroethylene is incapable of polymerization.

Tetrachloroethylene, $CCl_2=CCl_2$, can be synthesized by removing one mole of chlorine from hexachloroethane (a by-product in the chlorination of ethylene and acetylene) under the action of zinc or by heating with aluminium chloride:

$$CCl_3-CCl_3 \xrightarrow[-Cl_2]{} CCl_2=CCl_2$$

Tetrachloroethylene shows no tendency to polymerize either.

The most important of the fluorine derivatives of ethylene are **tetrafluoroethylene** (*tetrafluoroethene*), $CF_2=CF_2$, and **trifluorochloroethylene**, $CClF=CF_2$, which polymerize to give exclusively stable polymers.

Tetrafluoroethylene is made through the action of liquid hydrogen fluoride (or antimony trifluoride) on chloroform. The resulting difluorochloromethane is subjected to pyrolysis, the hydrogen chloride being eliminated and the remaining difluoromethylene radicals being coupled into tetrafluoroethylene:

$$2CHClF_2 \xrightarrow[-2HCl]{} [2CF_2] \longrightarrow CF_2=CF_2$$

The homologues of the halogen derivatives of ethylene are prepared either by the same method or by addition of hydrogen halides to the acetylenes:

$$R-C \equiv CH + HX \longrightarrow R-CX=CH_2$$

$$CH_2=CH-C \equiv CH + HCl \longrightarrow CH_2=CH-CCl=CH_2$$

or else by eliminating a hydrogen halide from saturated polyhalogen derivatives through their distillation with a small amount of ferric chloride (Freidlina):

$$R-CH_2-CCl_3 \xrightarrow[-HCl]{FeCl_3} R-CH=CCl_2$$

Unsaturated compounds containing a halogen at the saturated carbon atom are produced by the conventional methods; for example, allyl chloride is made from allyl alcohol (page 393):

$$CH_2=CH-CH_2OH+PCl_5 \longrightarrow CH_2=CH-CH_2Cl+POCl_3+HCl$$

As has been pointed out earlier (page 140), allyl chloride is produced commercially by the chlorination of propylene at a high temperature through the use of the L'vov reaction. Under these conditions the reaction involves only the substitution into the methyl group.

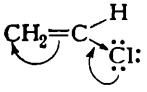
The halogen derivatives of acetylene can be obtained by eliminating a hydrogen halide from a symmetrical ethylene dihalide by the action of alkali:

$$XCH=CHX \xrightarrow[-HX]{} HC \equiv CX$$

A. Properties of Halogen Derivatives of Olefins

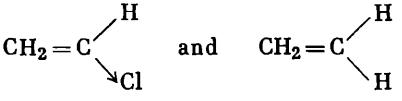
Compounds that contain a halogen linked to a doubly bound carbon atom sharply differ from those in which the halogen is joined with a saturated carbon atom.

The chlorine in vinyl chloride ($CH_2=CHCl$), vinylidene chloride ($CH_2=CCl_2$) and in dichloroethane ($ClCH=CHCl$), just as the bromine and iodine in the corresponding position, is hardly capable of entering into the exchange reactions typical of alkyl halides. This is accounted for by the weak mesomeric effect operating in the direction opposite to the ordinary polarization of the $\overset{\delta+}{C}-\overset{\delta-}{Cl}$ bond (which decreases the negative charge on Cl and the positive charge on C). This can be represented by the following schemes:



or $CH_2=CH-Cl \longleftrightarrow \bar{C}H_2-CH=\overset{+}{Cl}$

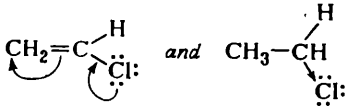
Here the curved arrows signify the mesomeric shift of the electrons and the straight arrow indicates the polarization. It should be emphasized that the straight-arrow symbolism is used for a comparison of vinyl chloride with ethylene:



From this comparison it follows that the carbon atom adjacent to the negative chlorine must bear a high positive charge.

The curved-arrow notation is utilized for comparing vinyl chloride with saturated chlorine derivatives, such as ethyl chloride, in

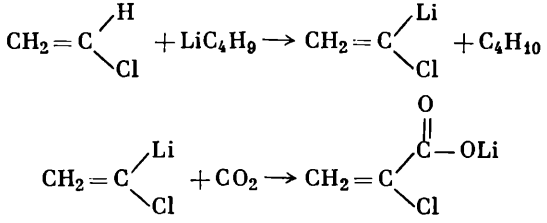
which there is no interaction between the electron pairs of chlorine and the electrons of the π-bond (absent in the alkyl halide molecule):



Partial (weak) donation of the free electron pair of chlorine for sharing with the neighbouring carbon (+*M* effect) cannot neutralize the positive charge of that carbon. But this results in the formation of a partial double bond between chlorine and carbon and in the shortening of the C—Cl distance as compared with alkyl halides and also in the partial supply of the π-electron olefinic bond to the extreme carbon atom (as compared with the case involving no interaction with chlorine such as that described above). Both carbon atoms, however, remain positively charged, though to a lesser degree than if no +*M* effect of chlorine were operating. The positive charge on carbon atoms is created by the powerful attraction of electrons by the cnlorine atom (the straight arrow in C → Cl).

All that has been described reduces the dipole moment of the molecule as a whole (it is equal to 1.5 D for vinyl chloride and to ca. 2 D for ethyl chloride), and, in particular, renders the bond between chlorine and carbon less polar and less reactive towards nucleophilic attacks, say, towards the attack of groups such as OH^- and CN^-. In other words, the chlorine becomes less mobile, i.e., less capable of exchange.

The statement that the carbon adjacent to chlorine bears a certain positive charge is confirmed by the experiment performed by Köbrich who carried out the following reaction through the action of butyl-lithium on vinyl chloride at about —100°C:

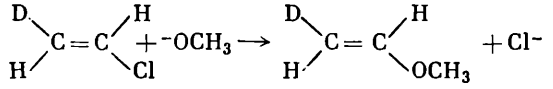


The elimination, under the action of a strong base, of the hydrogen atom adjacent to chlorine in the form of a proton which combines with the butyl residue into butane clearly points to the positive charge of the carbon atom bearing the chlorine.

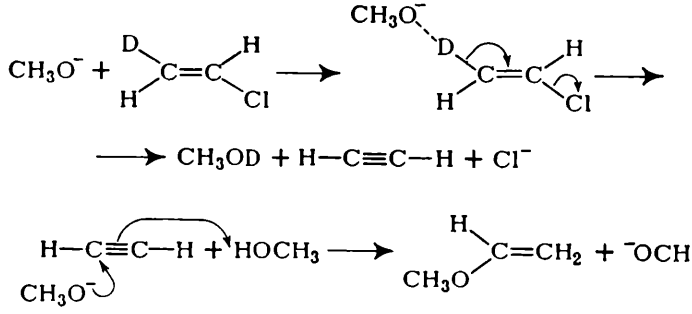
Thus, under ordinary conditions the halogen in vinyl halides is not substituted by nucleophilic particles. Under vigorous conditions involving the action of strong bases—nucleophilic agents (KOH,

KOR), the elements of a hydrogen halide are eliminated and a triple bond is formed; this is accompanied by a substitution reaction. Substitution products (for example, ethyl vinyl ether resulting from the interaction of vinyl chloride with sodium ethylate) could in principle be obtained in two ways: by the addition of a nucleophile to acetylene and by the direct attack of vinyl chloride and displacement of the halide anion. With the aid of deuterium labelling (deuteration) it has been shown that both mechanisms are realized simultaneously.

To prove this, *trans*-deuterochloroethane was introduced into reaction with sodium methylate. If the reaction proceeds as a direct exchange, deuterated methoxyethylene must result since the carbon atom that carries deuterium remains intact:

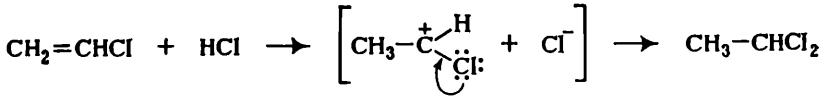


But if the elimination occurs first, undeuterated acetylene must form. The *trans*-elimination reaction is a more advantageous process since the only by-product formed is ordinary acetylene. The addition of the methylate to acetylene must lead only to a deuterated ether:



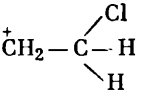
In practice, both a deuterated and an ordinary ether are formed in the ratio of 1.4:1, i.e., the direct replacement of the halogen atom predominates.

The addition of hydrogen chloride to vinyl chloride takes place according to the equation



but the attack of a proton on the carbon atom remote from chlorine does not prove that this carbon atom is charged. The point is that

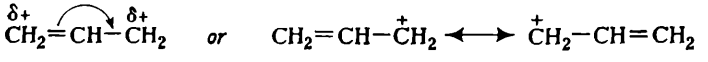
the transiently formed cation (in square brackets) is energetically more favourable than the isomeric intermediate cation



which would have formed if the addition had proceeded in the opposite direction (to the side of formation of $ClCH_2—CH_2Cl$). This means that the activation energy of the first reaction is much lower than that of the latter. This stability of the intermediate cation is achieved also owing to the participation of the electron pairs of chlorine (see above).

On the contrary, the halogen in alkyl halides (and in their homologues as well) shows an enhanced tendency towards exchange reactions.

This is associated with the ability of allyl chloride and its analogues and homologues to undergo electrolytic dissociation (no matter how little it is dissociated, it does so to a much higher degree than alkyl halides), which in its turn is the result of the high stability of the allyl cation as compared with the alkyl cation. Owing to the mesomeric effect, the positive charge of the allyl cation is not localized on a saturated carbon but is partly suppressed by the transfer of the electrons of the double bond, as a consequence of which the partial δ_+ charge on the extreme unsaturated carbon atom is exposed. Thus, the positive charge is distributed between the two extreme carbon atoms of the allylic system, which become completely equivalent:



Like all the phenomena of mesomeric (resonance) equilibration of electron density, this is accompanied by a decrease in the energy of the system and by stabilization.

Experiments devoted to the replacement of a halogen in less symmetric homologues of allyl halides or in allyl halides with a labelled carbon (^{14}C) show that such an exchange involves, quite frequently and even customarily, an allylic rearrangement (**Preveaux**), as a result of which the entering group (the one that replaces the halogen) becomes attached to the third atom of the system rather than to the atom with which the halogen was linked:

$$CH_2=CH-{}^{14}CH_2Cl+KCN \longrightarrow NC-CH_2-CH={}^{14}CH_2+KCl$$

In those cases where the exchange of an allyl halide occurs as a a unimolecular reaction, i.e., when first the allyl halide undergoes electrolytic dissociation (the slow rate-determining step of the reac-

tion) and then the allyl cation quickly combines with the anion, the latter adds on, with equal probability, to both extreme carbons and a mixture of the two products is formed:

$$CH_2=CH-{}^{14}CH_2-CN \qquad \text{and} \qquad NC-CH_2-CH={}^{14}CH_2$$

The allylic rearrangement however takes place, and completely at that, also in those cases when the reaction is second order, i.e., when the rate-determining step is the collision of two molecules of the reagent. In this case, it is easier for the anion that attacks the molecule to attack the extreme carbon atom with its δ_+ charge than the carbon attached to the halogen, this carbon being shielded by the negative charge of the halogen. Attacking the extreme carbon with a δ_+ charge, the anion, due to the easy polarizability of the π-bond, moves the electrons of this bond toward the halogen-carrying carbon and expels the halogen in the form of an anion:

$$:N\equiv\overset{\curvearrowright}{C}: \quad \overset{\delta+}{\underset{\displaystyle R}{CH}}=CH-CH_2-\overset{\curvearrowright}{\underset{\cdot\cdot}{Cl}}: \longrightarrow :N\equiv C-\underset{\displaystyle R}{CH}-CH=CH_2 + Cl^-$$

The system operates as an individual entity with conjugated C=C and C—Cl bonds (π,σ-conjugation). Formally, such an attack may be described as a 1,4-addition analogous to the addition to π,π-conjugated systems:

$$N\equiv\overset{\curvearrowright}{C}: \quad \overset{1}{\underset{\displaystyle R}{CH}}=\overset{2}{CH}-\overset{3}{CH_2}-\overset{4}{\underset{\cdot\cdot}{Cl}}: \; Na^+ \longrightarrow N\equiv C-\underset{\displaystyle R}{CH}-CH=CH_2 + NaCl$$

Just as in the case of 1,4-addition to π,π-conjugated systems, the 1,2 and 3,4 bonds are ruptured here (in our case, 3,4 is a single C—Cl bond and therefore Cl is split off) and a π-bond is formed in the 2,3 position.

The possibility has relatively recently been discovered of preparing vinylmagnesium halides from vinyl halides, for which purpose, according to the Normant method, use is made of a cyclic ether—tetrahydrofuran—in place of the ether in this Grignard reaction.

B. Uses of Halogen Derivatives of Olefins

These compounds are valuable non-inflammable solvents (trichloroethylene, $CHCl=CCl_2$) and are also used as intermediates in industrial syntheses. For example,

$$ClCH=CCl_2 + 2H_2O \xrightarrow{H_2SO_4} ClCH_2-C\begin{matrix}=O\\ \diagdown OH\end{matrix} + 2HCl$$

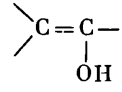
They are mainly utilized as monomers for polymerization into plastic materials. Such application requires only compounds in which the double bond resides at the end of the molecule at the group CH_2 or CF_2. Examples are $CH_2=CHCl$, $CH_2=CCl_2$, $CFCl=CF_2$, $CH_2=$ $=CCl-CH=CH_2$, $CH_2=CH-CCl_3$.

Especially wide use is made of the polymers of vinyl chloride (polyvinyl chloride), which are made by homolytic polymerization. When plasticized with the esters of sebacic or other dibasic acids, they are utilized as substitutes for leather, for the manufacture of gas pipes, fibres which have found technical application, etc., and also as pigment-carriers in paints and varnishes. Vinylidene chloride is used in the form of a polymer or copolymer with vinyl chloride for insulation of cables.

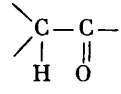
Tetrafluoroethylene subjected to homolytic polymerization gives a polymer called Teflon which has a surprisingly high chemical stability (for which reason it is called "organic platinum"). It is resistant to the most concentrated acids and alkalis at a rather high temperature. It is completely stable to the action of oxidizing agents and aqua regia, and withstands temperatures up to 330°C. Tetrafluoroethylene is used in the manufacture of chemical equipment and in the instrument-building industry for making components which must be resistant to chemically aggressive media. Because of the extremely low polarizability of the fluorine bound covalently with carbon, very weak van der Waals forces are exhibited by Teflon, each molecule of which is surrounded by such fluorine atoms, and therefore this material is not wetted by liquids and is not affected by any of the existing solvents. Polychlorotrifluoroethylene forms plastics similar to Teflon.

3.9. Unsaturated Alcohols and Their Ethers and Esters

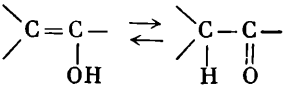
Olefins or alkenes cannot carry a hydroxyl group at the doubly bound carbon. Structures such as



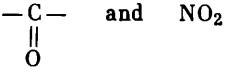
are unstable and isomerize into



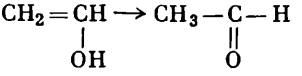
(the Eltekov-Erlenmeyer rule). Only in certain specific cases (Vol. II) is such an isomerization reversible to a noticeable degree, in which case we deal with tautomeric equilibrium:



For structures in which the unsaturated carbon atom that does not carry a hydroxyl is not joined to electron-withdrawing groups such as, for example,

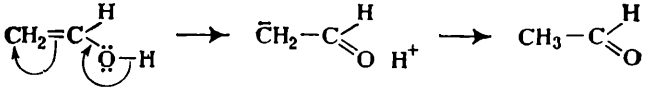


the Eltekov-Erlenmeyer rule is completely valid. Therefore, vinyl alcohol and its homologues do not exist. When attempts are made to prepare them, they rearrange to acetaldehyde (and correspondingly into its homologues):



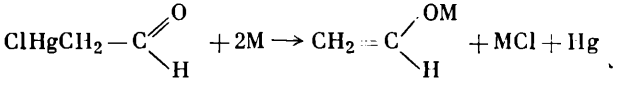
or to ketones.

This rearrangement is caused by the same mesomeric effect which operates in vinyl chloride. In this case, however, this effect operates to the full, until all the electron pairs are completely transferred, and is thus a $+T$ effect (pages 239 and 372):



This effect tends to remove the hydroxyl hydrogen as a proton and provides, at the second unsaturated carbon atom with its δ-charge, a convenient site for attack by the hydrogen ion. As a result, an isomerization takes place and the proton is transferred to the carbon.

Alkoxides and also ethers and esters of vinyl alcohol, however, not only exist but, as in the last two cases, are even utilized on an industrial scale as monomers. Of course, they have to be made by indirect routes. The action of metallic lithium or sodium in solution in liquid ammonia on the mercury derivative of acetaldehyde yields the alkoxides of vinyl alcohol (I. F. Lutsenko):



where M = Li or Na.

These alkoxides (more precisely, enolates since vinyl alcohol is also called ethenol and its metallic derivatives are accordingly ethenolates) are highly unstable and all attempts to make them enter into alkylation or acylation reactions end with the formation of aldol and crotonaldehyde with acetaldehyde, which is isolated by protolysis with a solvent (an alcohol or water).

Vinyl ethers and esters are made, as has already been mentioned (see page 355), on an industrial scale by addition of alcohols (in the presence of KOH) and carboxylic acids [in the presence of mercury(II), cadmium and zinc salts] to acetylene:

$$ROH + HC \equiv CH \xrightarrow{KOH} RO-CH=CH_2$$

$$R-\underset{\underset{O}{\|}}{C}-OH + HC \equiv CH \xrightarrow{M^{2+};\ 70\ ^\circ C} R-\underset{\underset{O}{\|}}{C}-O-CH=CH_2$$

Mention should also be made in this respect of the action of acetic anhydride on ketones in the presence of sulphuric acid:

$$CH_3-\underset{\underset{O}{\|}}{C}-CH_3 + CH_3-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow{H^+}$$

$$\rightarrow CH_2=\underset{\underset{CH_3}{|}}{C}-O-\underset{\underset{O}{\|}}{C}-CH_3 + CH_3-\underset{\underset{O}{\|}}{C}-OH$$

and of the action of ketene on acetaldehyde:

$$CH_3-\underset{\underset{O}{\|}}{C}-H + CH_2=C=O \rightarrow CH_2=\underset{\underset{O-\underset{\underset{O}{\|}}{C}-CH_3}{|}}{CH}\ O$$

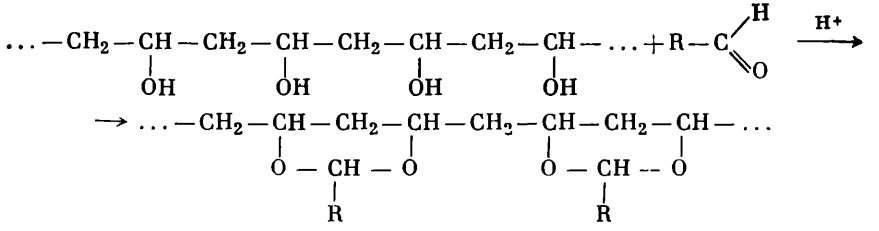
An especially important vinyl ester is **vinyl acetate** which polymerizes homolytically to polyvinyl acetate. The latter is used for the production of transparent plastic materials, triplex (glueing of layers of silicate glass), and also of polyvinyl alcohol by the hydrolysis of polyvinyl acetate:

$$\ldots-CH_2-\underset{\underset{CH_3C-\underset{\underset{O}{\|}}{O}}{|}}{CH}-\left[-CH_2-\underset{\underset{CH_3C-\underset{\underset{O}{\|}}{O}}{|}}{CH}-\right]_n-\ldots \xrightarrow{H_2O}$$

$$\rightarrow \ldots-CH_2-\underset{\underset{OH}{|}}{CH}-\left[-CH_2-\underset{\underset{OH}{|}}{CH}-\right]_n-\ldots-$$

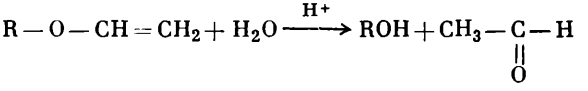
Polyvinyl alcohol finds application for preparing important polymeric materials through acetal formation by aldehydes, in particu-

lar, by butyraldehyde (polyvinyl butyral):

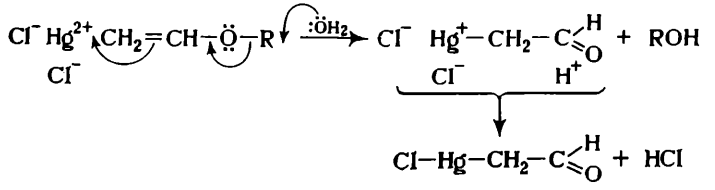


Wide use is also made of copolymers of vinyl acetate with vinyl chloride.

Alkyl vinyl ethers have been obtained independently by Favorsky and Shostakovsky and by Reppe (page 355). Their specific feature is the ease with which their hydrolysis takes place in acid solution (in contrast to dialkyl ethers), acetaldehyde being produced instead of its isomer—vinyl alcohol:



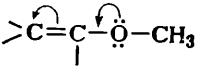
The reaction may be thought to begin with the attack by H^+ on the extreme unsaturated carbon atom. At least, such is the attack by mercuric ion (A. N. Nesmeyanov, I. F. Lutsenko), which converts alkyl vinyl ether to acetaldehyde replaced in the alpha position by the ClHg group:



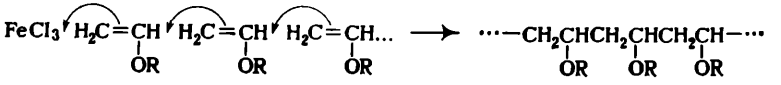
The synthesis of vinyl ether from acetylene and its hydrolysis to acetaldehyde (these reactions require no mercury catalyst which is used in the direct hydration of acetylene to acetaldehyde by the Kucherov method) have been proposed as methods of preparing acetaldehyde from acetylene by indirect hydration (A. E. Favorsky, M. F. Shostakovsky).

When heated alkyl vinyl ethers undergo a Claisen rearrangement to form aldehydes*

due to the strong T effect of the p,π-conjugated group



Vinyl ethers, say, vinyl butyl ether, polymerize readily too, but predominantly heterolytically, the reaction being initiated by Lewis acids, for example, by $FeCl_3$:

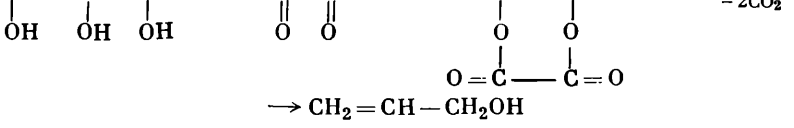


This reaction gives liquid viscous polymers used as thickeners. Vinyl ethers also form solid copolymers as a result of the peroxide-initiated homolytic polymerization.

Allyl alcohol, $CH_2=CH-CH_2OH$, is the simplest representative of unsaturated alcohols with the hydroxyl group being remote from the double bond; it differs little from alkanols in the properties of the hydroxyl group. It is quite natural that the presence of a double bond is responsible for its unsaturated character and a number of reactions which are familiar to us. An industrial method of preparing allyl alcohol is the hydrolysis of allyl chloride which is produced by chlorination of propylene at a high temperature:

$$CH_2=CH-CH_3+Cl_2 \xrightarrow[-HCl]{} CH_2=CH-CH_2Cl \xrightarrow{OH^-} CH_2=CH-CH_2OH$$

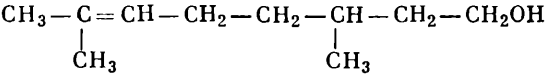
Formerly, allyl alcohol was made by heating glycerol with oxalic acid (the resulting ester loses on pyrolysis the elements of the oxalate group in the form of $2CO_2$):



In the vegetable world there occur a number of unsaturated alcohols having the skeleton of isoprenoid compounds, i.e., dimeric,

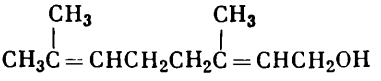
* Compare with the rearrangement of allylphenols (see Volume IV).

trimeric, tetrameric, etc., isoprene. We shall only cite an alcohol with one double bond—**citronellol**

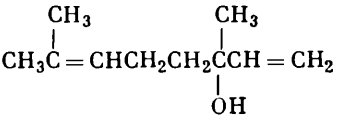


This is a fragrant liquid, a constituent of rose oil, citronella oil and other essential oils.* Its structure is established by ozonization.

Two double bonds are contained in **geraniol** and **linalool**, an isomer of geraniol:



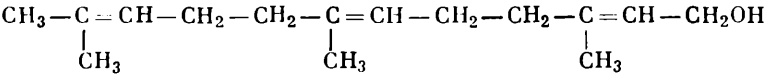
Geraniol



Linalool

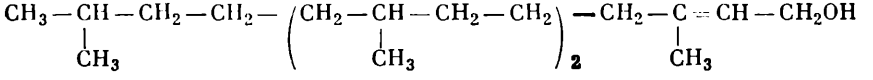
Geraniol is the chief constituent of geranium oil (from which it may be obtained) and is responsible for its pleasant odour. It is also contained in rose oil. On ozonization geraniol forms levulinic aldehyde (just like natural rubber; see page 379), acetone, and glycolic aldehyde, which proves its structure. Linalool has an odour similar to that of lily of the valley and is used in the perfume industry as such and also in the form of esters (linalool acetate). It occurs in lavender, bergamot, and coriander essential oils. Linalool can be obtained from geraniol by allylic rearrangement (page 387).

Farnesol is a constituent of ambrette-seed oil and has a lily-of-the valley odour. It has the following structure:



It is used in perfumery.

Phytol has the structure



and enters in the form of an ester into the composition of the chlorophyll molecule (see Volumes III and IV).

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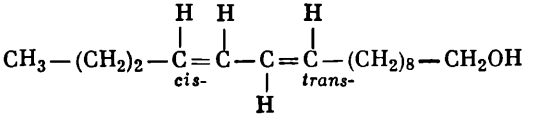
* The essential oils of flowers (or leaves) are obtained by steam distillation of their volatile constituents. The lighter layer of the oil is then separated from the water.

When studying the substances secreted by female butterflies and serving for attracting males by their smell, Butenandt isolated an unsaturated alcohol, *bombykol*, from female silkworm:



Butterflies feel its odour at an enormous distance.

3.10. Acetylenic Alcohols and Ethers

These compounds are of no great importance and have been studied relatively little. We shall mention only **propargyl alcohol**, $CH{\equiv}C{-}CH_2OH$, which can be obtained most simply by the Reppe method (page 357):

$$HC \equiv CH + CH_2O \xrightarrow{CuC \equiv CCu} HC \equiv C{-}CH_2OH$$

It possesses an ordinary alcoholic function and is capable of allylic rearrangement upon replacement of the hydroxyl group; having an acetylenic hydrogen, propargyl alcohol can exchange it, like acetylene, for metals, say, for silver and copper.

Butynediol, $HOCH_2{-}C{\equiv}C{-}CH_2OH$, has been described on pages 359 and 364.

Alkyl ethynyl ethers were first obtained by M. N. Shchukina who used vinyl ethers as a starting material:

$$CH_2{=}CH{-}OR + Br_2 \longrightarrow CH_2Br{-}CHBr{-}OR \xrightarrow{C_2H_5ONa} CH \equiv C{-}OR$$

They are prepared (after Jacobs) by the action of zinc dust in alcohol on the acetals of dibromoacetaldehyde and by splitting off HBr from the alkyl bromovinyl ether formed:

$$Br_2CH{-}CH(OR)_2 \xrightarrow{Zn;\ C_2H_5OH} BrCH{=}CH{-}OR + Zn\begin{matrix}Br\\OR\end{matrix}$$

$$BrCH{=}CH{-}OR \xrightarrow{C_2H_5ONa} CH \equiv C{-}OR$$

These compounds have found application in diene synthesis since they are easily condensed with dienes.

3.II. Unsaturated Carbonyl Compounds

A. Carbonyl Compounds with the Olefinic Bond

In carbonyl compounds, the double bonds (an olefinic and a carbonyl bond) may be conjugated, in which case they are separated by one single bond and the entire grouping has the form

$$-C=C-C=O$$

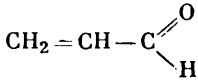
or isolated, i.e., separated by a large number of single bonds.

Aldehydes and ketones with an isolated carbonyl and olefinic π-bond being far apart from each other are obtained by the usual methods of synthesizing aldehydes and ketones with the only difference that a corresponding unsaturated reagent is used. Their properties may be regarded as a combination of the properties of carbonyl compounds and olefins.

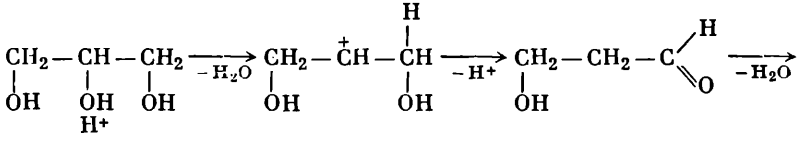
Only carbonyl compounds with conjugated bonds are of interest as far as the specific features of synthesis and reactions are concerned. Therefore we shall consider only these compounds.

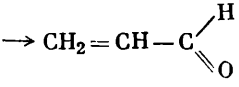
(a) *Synthesis of Unsaturated Aldehydes with Conjugated* C=C *and* C=O *Bonds*

A special place in this series of aldehydes is occupied by the first member of the series—**acrolein (propenal)**



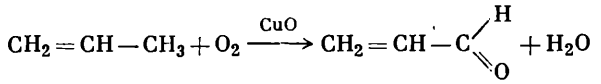
The long-known method of preparing acrolein—the dehydration of glycerol—is accomplished by heating glycerol up to 200°C with alkali metal hydrosulphates, for example, with $KHSO_4$. The reaction is clear from the equation:



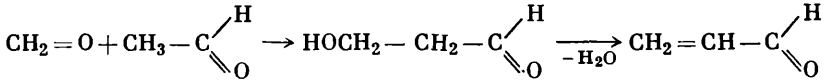


New routes to acrolein are much more important technically. These include:

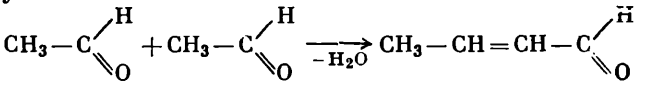
(a) the oxidation of propylene by the air over a CuO catalyst at 350-400°C and a pressure a little above the atmospheric:



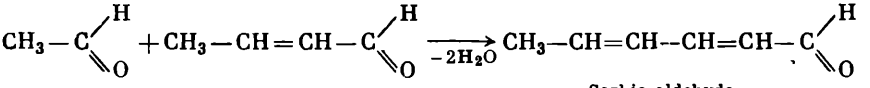
(b) the condensation of formaldehyde with acetaldehyde over silica gel (alkaline) with the simultaneous dehydration (300°C) of the resulting β-hydroxypropionaldehyde:



The homologues of acrolein are prepared by the croton condensation of aldehydes (page 188), for example, **crotonaldehyde** from acetaldehyde:



As has already been mentioned (page 371), owing to the transmitting conjugated system of bonds C=C—C=O crotonaldehyde has an active methyl group (active hydrogens) and condenses in its turn with aldehydes according to the croton-type mechanism:

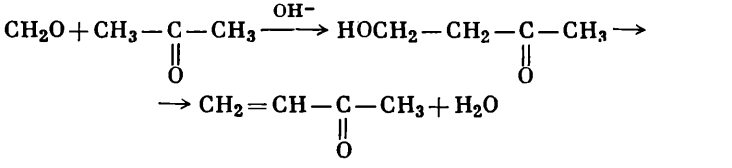


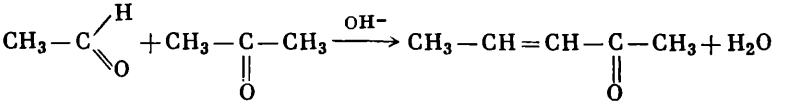
Sorbic aldehyde

The mobility of the hydrogens of the methyl group is retained by sorbic aldehyde too.

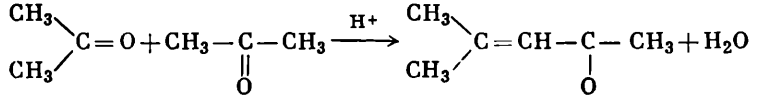
(b) *Synthesis of Unsaturated Ketones*

These compounds are made by way of condensation of aldehydes with ketones (aldol condensation followed by crotonation) or of ketones with ketones. In reactions between aldehydes and ketones, use is made of an alkaline catalyst: a little alkali or a secondary amine—piperidine (see Volume III, "Heterocyclic Compounds"):

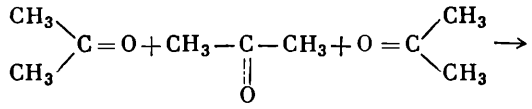


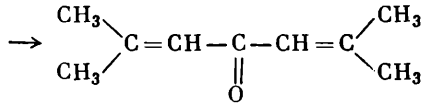


When ketones are reacted with each other, sulphuric acid or a Lewis acid is employed:



Mesityl oxide





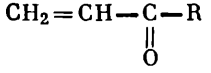
Phorone

(c) *Properties of Carbonyl Compounds with Conjugated Double Bonds*

Such carbonyl compounds are highly reactive and, as it usually happens in such cases, have a pungent smell.

Especially aggressive is acrolein which has such a strong lachrymatory effect that during the World War I it was used in the French Army as a lachrymator. Kitchen fumes are also lachrymal because of the presence of small amounts of acrolein resulting from the decomposition of glycerol and its esters (fats) in the pyrolysis on the pan.

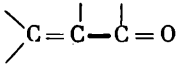
Vinyl ketones of the type



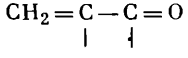
have a rather pungent odour as well.

Ketones of the type of mesityl oxide and phorone possess a relatively pleasant smell, just as the higher unsaturated aldehydes.

The more common property of the systems



is the increased activity of the olefinic bond in addition reactions, in particular, in reactions of olefinic polymerization (vinyl polymerization); this refers in the first place to systems with an unsubstituted methylene group, i.e.,



Such substances as vinyl ketones

$$CH_2=CH-\overset{\overset{O}{\|}}{C}-R$$

serve, for example, as monomers for producing polymers that have found practical application. The tendency of acrolein to polymerize is so great that for a long time it could not be stored (this was especially important in connection with its military application).

The French chemist Charles Moureu disclosed the relationship between the oxidation and polymerization of acrolein and showed that the introduction of small amounts of oxidation inhibitors (say, hydroquinone, see Volume III) stops not only its oxidation but its polymerization as well. This is accounted for by the fact that the oxidation gives rise to peroxides, some of which (as well as their decomposition products) have the properties of free radicals and are thus capable of initiating polymerization.

The relation between the oxidation and polymerization of conjugated carbonyl compounds is of general importance. In the case of acrolein it is expressed as follows:

A step in a chain oxidation reaction (one of many possible)

$$CH_2=CH-\overset{\overset{O}{\|}}{C}-H + Fe^{3+} \longrightarrow CH_2=CH-\overset{\overset{O}{\|}}{\underset{\bullet}{C}} + H^+ + Fe^{2+}$$

An oxidation initiator (one of many possible)

$$CH_2=CH-\overset{\overset{O}{\|}}{\underset{\bullet}{C}} + O_2 \longrightarrow CH_2=CH-\overset{\overset{O}{\|}}{C}-O-O\cdot$$

$$CH_2=CH-\overset{\overset{O}{\|}}{C}-H + CH_2=CH-\overset{\overset{O}{\|}}{C}-O-O\cdot \longrightarrow$$

$$\longrightarrow CH_2=CH-\overset{\overset{O}{\|}}{\underset{\bullet}{C}} + CH_2=CH-\overset{\overset{O}{\|}}{C}-OOH$$

$$CH_2=CH-\overset{\overset{O}{\|}}{C}-OOH + CH_2=CH-\overset{\overset{O}{\|}}{C}-H \longrightarrow 2CH_2=CH-\overset{\overset{O}{\|}}{C}-OH$$

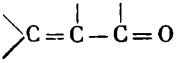
$$CH_2=CH-\overset{\overset{O}{\|}}{\underset{\bullet}{C}} + nCH_2=\underset{\underset{CHO}{|}}{CH} \longrightarrow CH_2=CH-\overset{\overset{O}{\|}}{C}-CH_2-\underset{\underset{CHO}{|}}{CH}-\left(CH_2-\underset{\underset{CHO}{|}}{CH}\right)_{n-1}-\ldots$$

An initiator of polymerization (one of many possible)

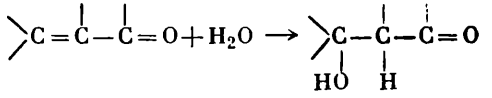
The role of the oxidation inhibitor (antioxidant) and polymerization inhibitor consists in the capture and immobilization of free radicals (the process is discussed in more detail in Volume III).

The acrolein stabilized by hydroquinone can be stored for a very long period of time.

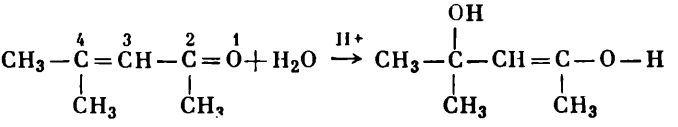
All the conjugated systems



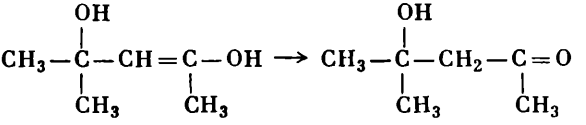
are capable of adding water in acid medium, the addition taking place contrary to Markovnikov's rule:



There is ground to believe that this order of addition of water, and also of hydrogen halides and acids, is due to 1,4-addition (page 368), for example,

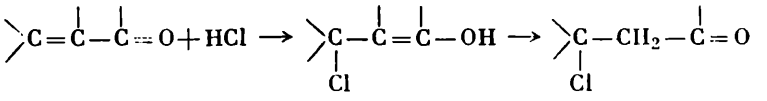


The hydrogen ion adds on to the carbonyl oxygen and the hydroxyl ion OH^- to the remote olefinic carbon. According to the Eltekov-Erlenmeyer rule the resulting molecule is unstable and undergoes rearrangement:



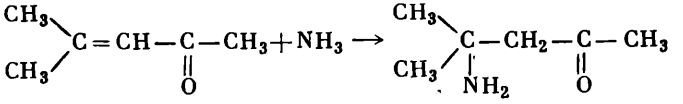
As a result of this, the carbonyl is regenerated and outwardly the addition seems to have occurred as if at the C=C bond.

The addition of HCl proceeds in an analogous manner:

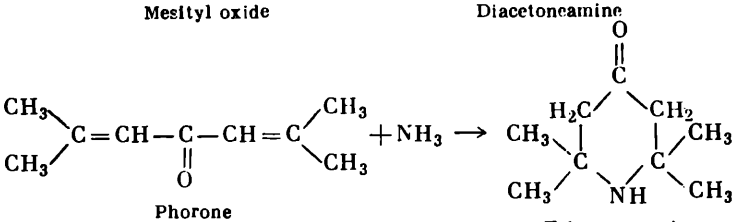


Ammonia too adds on readily to unsaturated ketones with a conjugated bond. For mesityl oxide and phorone the reactions take

place as follows:

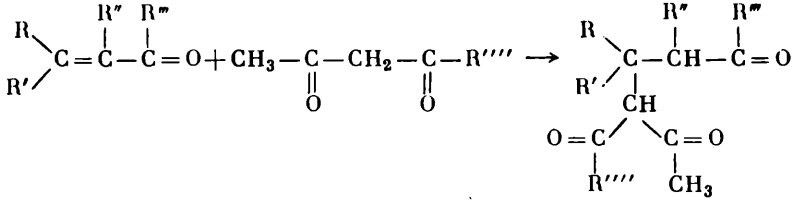


Mesityl oxide — Diacetoneamine



Phorone — Triacetoneamine (2,2,6,6-tetramethyl-4-piperidone)

An important reaction in organic chemistry is the Michael reaction which consists in the addition of compounds containing a mobile hydrogen to unsaturated conjugated carbonyl compounds in alkaline solution; an example is the addition of malonic ester, the esters of β-keto acids and also of β-diketones according to the following scheme:

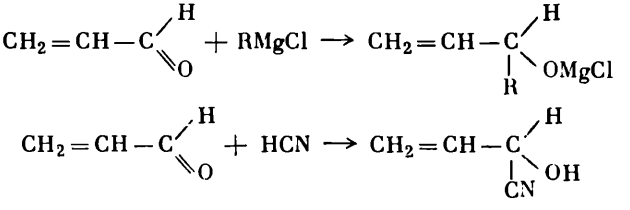


According to the Michael reaction the anion of a diketone, ester of a β-keto acid, or malonic ester, attacks the β-carbon atom of the unsaturated carbonyl compound.

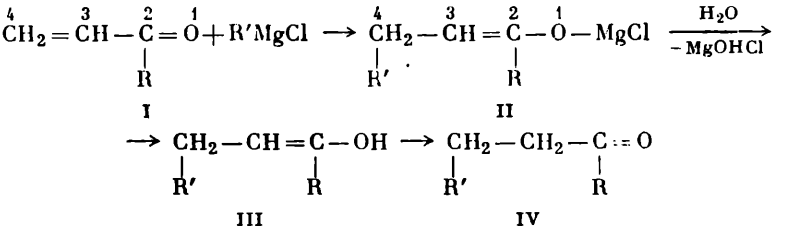
As a matter of fact, the addition of hydrocyanic acid falls in this category of reactions (see below).

From what has been said above it may be seen that there is a certain analogy between the conjugated systems C=C—C=O and C=C—C=C (page 367).

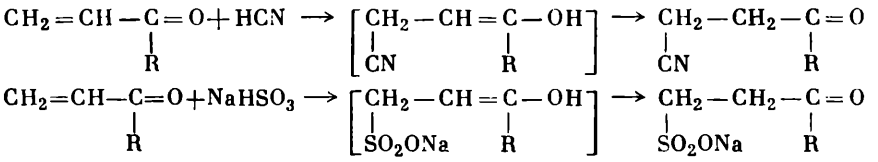
Especially interesting is the course of reactions with reagents capable of adding on to the carbonyl double bond. This is a point of sharp difference between aldehydes and ketones. Aldehydes react normally at their carbonyl group, for example,



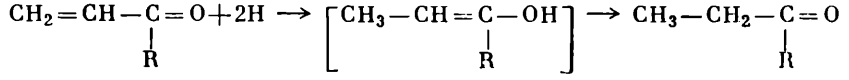
Ketones often (though not always) react, adding the reagent in the 1,4-positions:



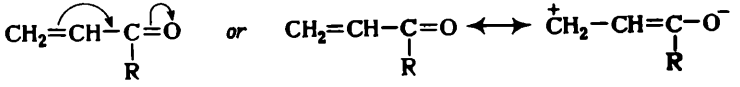
Thus, the hydrolysis of the addition product of a Grignard reagent to an unsaturated ketone is followed by the formation (via the unstable enol form III) of the saturated ketone IV. Upon addition of a Grignard reagent in the 1,4-positions the double bond migrates, as is always the case (page 368), to the 2,3-positions. This has been proved by the ozonization of enolates (Kohler). By analogy, the same course of the reaction—the addition at the 1,4-positions—is also assumed for reagents with a mobile hydrogen (HCN, $NaHSO_3$, etc), in which case it is impossible to isolate the initially formed enol:



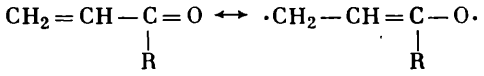
In contrast to the isolated olefinic bond but like the conjugated system C=C—C=C, unsaturated aldehydes and ketones are reduced by nascent hydrogen. This reduction gives saturated carbonyl compounds:



that is, in this case too it seems as if the hydrogen were added to the C=C bond, leaving the C=O bond intact. It should be noted that, except this obviously homolytic reaction, all other reactions are heterolytic: the quaternary (carbon) atom of the system undergoes nucleophilic attack (CN^-, HSO_3^-, OH^-), which is not characteristic of olefins (ordinarily the addition to olefins begins with the electrophilic attack of Br_2, H^+, Hg^{2+}, etc.). All this indicates that in this particular case the conjugation may be expressed by symbols



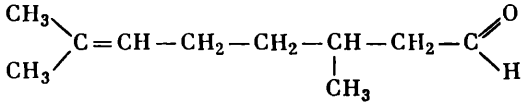
rather than as



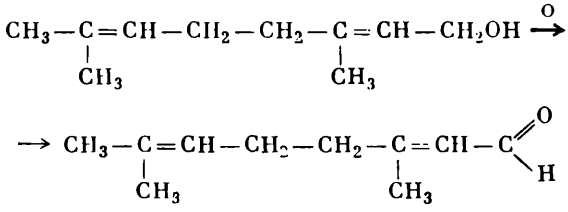
that is, the conjugation has a heterolytic character. In other words, the overlap of the orbitals of π-electrons takes place so that they are concentrated, to a larger extent, on the more negative oxygen; this non-uniform distribution of electrons is sharply increased at the moment of attack (the dynamic conjugation or tautomeric effect).

Of the unsaturated carbonyl compounds that occur in plants and are of industrial value (perfumery) mention should be made of citronellal and citral.

Citronellal is the aldehyde of citronella oil (nard, *Aralia racemosa*) and is also found in lemon oil and oil of eucalyptus*. It has the isoprenoid skeleton (see Volume III):



Citral (*geranial*) contains two olefinic bonds. It occurs in many essential oils (verbena oil, lemon oil, and especially in lemon-grass oil). Citral can also be obtained by gentle oxidation of geraniol (page 394):



This reaction shows a close relation between the two natural compounds.

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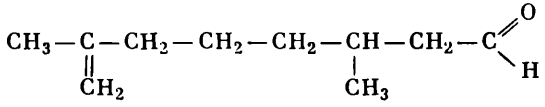
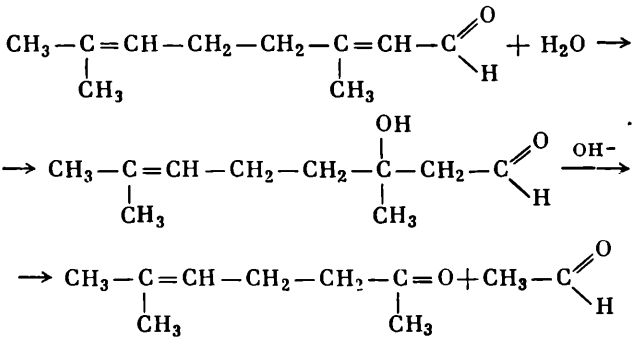
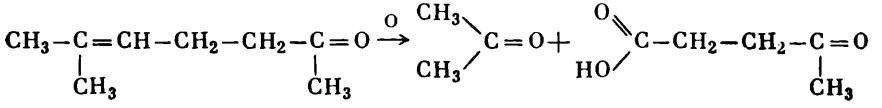
* These oils also contain an impurity which is difficult to separate:



On boiling in alkaline solutions citral decomposes into acetaldehyde and methylheptenone:

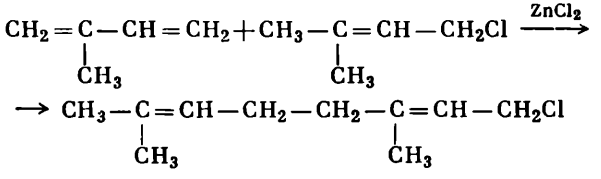


The first stage of the reaction is the hydration of the conjugated system C=C—C=O; the second stage is the reaction which is the converse of aldol condensation. The constitution of methylheptenone follows from its oxidation to acetone and levulinic acid (see Volume II):



These reactions give a clue to the structure of citral and also of geraniol.

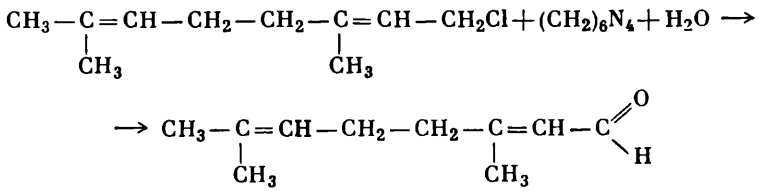
A.A. Petrov suggested the following synthesis of citral: to one molecule of isoprene there adds on, in the presence of zinc chloride, the product of 1,4-addition of hydrogen chloride to another isoprene molecule:



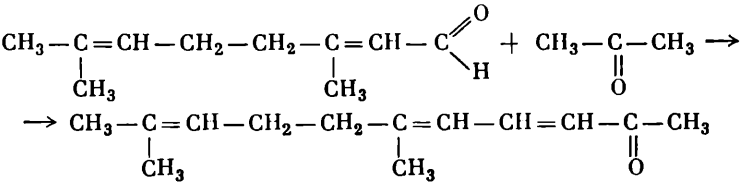
Geranyl chloride is formed, which on being boiled with an aqueous solution of urotropin (the Sommelet reaction*) is converted into an

* The mechanism of the Sommelet reaction (the urotropin oxidation of the $-CH_2Cl$ grouping to $-CH=O$) will be described in Volume IV.

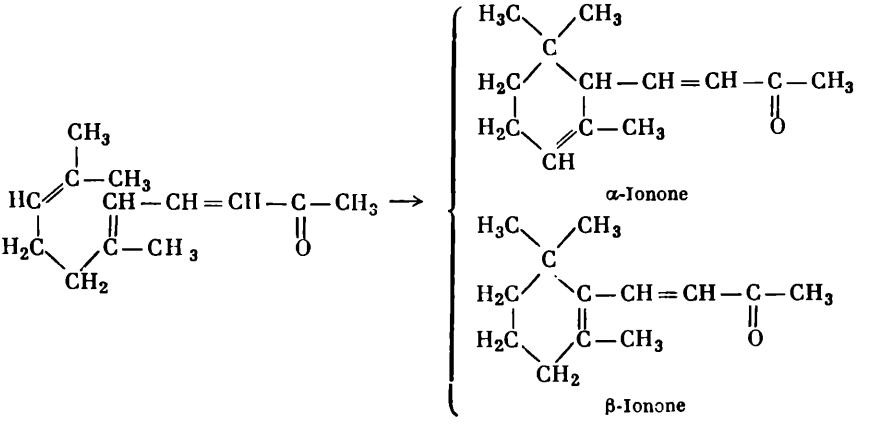
aldehyde—citral:



Citral enters into croton condensation with acetone, forming an unsaturated ketone—**pseudoionone**:



On being heated with acids, pseudoionone isomerizes to cyclic unsaturated ketones—**ionones** which are isomeric with each other:

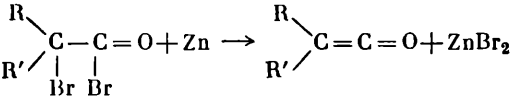


These ionones have the pleasant odour of violets and are widely used for the manufacture of scents. The ionones are close in structure to the natural fragrant substance found in the violet and orris root—**irone** (see Volume IV).

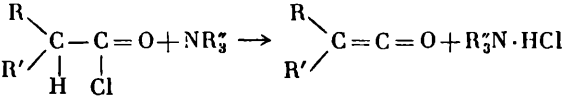
B. Ketenes

In 1905 Staudinger discovered a new class of unsaturated carbonyl compounds—ketenes with a characteristic grouping, C=C=O. They were prepared by elimination of bromine from the bromine

anhydrides of α-bromosubstituted acids by zinc:



or by dehydrohalogenation of acid chlorides by zinc or a tertiary amine:



Ketene (or keten), $CH_2=C=O$, the simplest member of this class of compounds, can be made by pyrolysis of acetone:

$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{500-600\,^\circ C} CH_2=C=O+CH_4$$

or acetic acid:

$$CH_3-\overset{\overset{O}{\|}}{C}-OH \xrightarrow{700\,^\circ C} CH_2=C=O+H_2O$$

Both these reactions are employed industrially for the production of ketene, which is then converted into acetic anhydride:

$$CH_3-\overset{\overset{O}{\|}}{C}-OH+CH_2=C=O \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-CH_3$$

Ketenes are also formed as a result of certain rearrangements (see Volume IV, "Rearrangements").

Ketene is a gas with b.p. −41°C and m.p. −135°C; dimethylketene, $(CH_3)_2C=C=O$, is a light-yellow liquid with b.p. 34°C and m.p. −98°C.

Ketenes may be regarded as a sort of acid anhydrides. Indeed, with water they are instantly converted into acids, with alcohols into esters, with ammonia and amines into amides and substituted amides, and with acids into acid anhydrides:

$$H_2C=C=O+H_2O \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-OH$$

$$H_2C=C=O+ROH \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-OR$$

$$H_2C=C=O+NH_3 \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-NH_2$$

$$H_2C=C=O+CH_3-\overset{\overset{O}{\|}}{C}-OH \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-CH_3$$

They also acylate the amides of acids, giving diacylamines (imides) and triacylamines at separate stages (K. A. Kocheshkov):

$$CH_3-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow[H_2SO_4]{CH_2=C=O;} \left(CH_3-\overset{\overset{O}{\|}}{C}\right)_2NH \xrightarrow[H_2SO_4]{CH_2=C=O;} \left(CH_3-\overset{\overset{O}{\|}}{C}\right)_3N$$

Ketenes also acylate carbonyl compounds with an unsubstituted α-methylene group. This reaction yields acyl derivatives of the enol form:

$$CH_2=C=O + CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{CH_3}{|}}{C}=CH_2$$

Ketenes readily undergo spontaneous dimerization into diketenes:

$$\begin{matrix} CH_2=C=O \\ + \\ CH_2=C=O \end{matrix} \longrightarrow \begin{matrix} CH_2=C-\!\!-O \\ | \quad | \\ CH_2-C=O \end{matrix}$$

from which ketenes can be regenerated by pyrolysis at 600°C.

The simplest diketene, whose formula is given above, is the β-lactone of the enol form of acetoacetic ester (see Volume II). When acted on by ethanol it is converted into acetoacetic ester, this providing a confirmation of its structure:

$$\begin{matrix} CH_2=C-\!\!-O \\ | \quad | \\ CH_2-C=O \end{matrix} + C_2H_5OH \longrightarrow \underset{\text{Ethyl acetoacetate}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-OC_2H_5}$$

The product of dehydration of malonic acid—bis-diketene, *carbon suboxide*, O=C=C=C=O, was mentioned on page 255.

3.12. Unsaturated Acids

A. Monobasic Acids of the Ethylene Series

Unsaturated acids of the type

$$-\overset{|}{C}=\overset{|}{C}-\overset{|}{C}=O \quad (OH)$$

with conjugated carbonyl and ethylene double bonds (α,β-unsaturated) differ sharply in methods of preparation and in properties from acids with isolated multiple bonds of the type

$$-\overset{|}{C}=\overset{|}{C}-(CH_2)_x-\overset{|}{C}=O \quad (OH)$$

The physical properties of the representatives of both types of acids are listed in Table 3.5.

TABLE 3.5. Acrylic Acid, Its Homologues and Derivatives

Formula	Acid	m.p., °C	b.p., °C	Density d_4^{20}	K_a (at 25°C)	Ester	b.p., °C	Density d_4^4
$CH_2=CH-COOH$	Acrylic	12.3	141.9	1.062 (at 16°C)	5.60×10^{-5}	Methyl	80.5	0.953
$CH_3-CH=CH-COOH$	Isocrotonic (*cis*-crotonic) or *cis*-β-methylacrylic	14-15	171.9 (decomp.)	1.0312 (d_4^{15})	—	Methyl	—	—
	Crotonic (*trans*--crotonic) or *trans*-β-methylacrylic	72.0	189	1.018 (d_4^{15})	2.03×10^{-5}	Methyl	120.7	0.944
$CH_2=C(CH_3)-COOH$	Methacrylic or α-methylacrylic*	16	163	1.015	—	Methyl	100	0.936
$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$	Oleic							
	cis-	14	286 (at 100 mm Hg)	0.895 (d_4^{18})	—	Methyl	217 (at 20 mm Hg)	0.879 (at 18°C)
	trans-, or elaidic	51.5	288 (at 100 mm Hg)	0.8510 (d_4^{79})	—	Methyl	213.5 (at 15 mm Hg)	0.872 (d_4^{15})
$CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7COOH$	Linoleic	−11; −5.2	230 (at 16 mm Hg)	0.9025	—	Methyl	207 (at 11 mm Hg)	0.889 (at 18°C)
$CH_3(CH_2CH=CH)_3(CH_2)_7COOH$	α-Linolenic	−11.3	230-232 (at 17 mm Hg)	0.9150	—	Methyl	—	—

The simplest and most important acids with conjugated bonds are acrylic acid and its homologues, α-methylacrylic, or methacrylic acid, and β-methylacrylic, or crotonic acid. To the first acid and the last there correspond aldehydes which we already know—acrolein and crotonaldehyde. Their kinship can be established by oxidation of these aldehydes to the corresponding acids by means of oxidizing agents which do not disturb double bonds, say, Fehling's solution.

Acrylic and methacrylic acids are of great technical importance. They can be produced by the following industrial methods.

Acrylic acid. 1. From ethylene chlorohydrin or ethylene oxide via the nitrile of β-hydroxypropionic acid (β-hydroxypropionitrile) by hydrolysis with simultaneous dehydration of the nitrile by concentrated sulphuric acid:

$$\left.\begin{array}{l} HOCH_2-CH_2Cl+KCN \\ H_2C\!-\!CH_2+HCN \\ \quad\diagdown\diagup\ O \end{array}\right\rbrace \longrightarrow \underset{\underset{OH}{|}}{CH_2-CH_2CN} \xrightarrow[H_2SO_4]{H_2O;} CH_2=CH-\underset{\underset{OH}{|}}{C}=O$$

2. By hydrolysis of acrylonitrile:

$$CH_2=CH-C\equiv N+2H_2O \xrightarrow{H_2SO_4} CH_2=CH-\underset{\underset{OH}{|}}{C}=O+NH_4HSO_4$$

Acrylonitrile is produced industrially by means of the following reactions:

$$H_2C\!-\!CH_2+HCN \longrightarrow HOCH_2-CH_2CN \xrightarrow[-H_2O]{} CH_2=CH-CN \qquad (1)$$

$$HC\equiv CH+HCN \xrightarrow{CuCl;\ NH_4Cl;\ HCl} CH_2=CH-CN \qquad (2)$$

$$2CH_2=CH-CH_3+{}^3/_2O_2+2NH_3 \longrightarrow 2CH_2=CH-CN+3H_2O \qquad (3)$$

reaction (3) being the oxidation of a mixture of propylene and ammonia by an insufficient amount of air over a catalyst (this is probably the most economical and promising route).

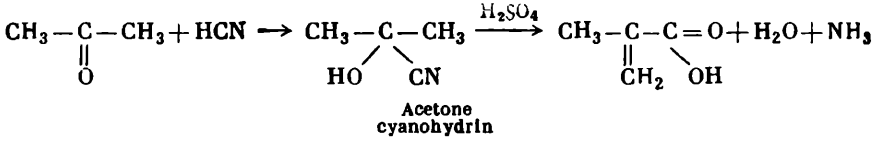
3. From acetylene by the Reppe reaction (see page 357):

$$HC\equiv CH+CO+H_2O \xrightarrow{Ni(CO)_4} CH_2=CH-\underset{\underset{OH}{|}}{C}=O$$

4. By the addition of phosgene to ethylene in the presence of $AlCl_3$:

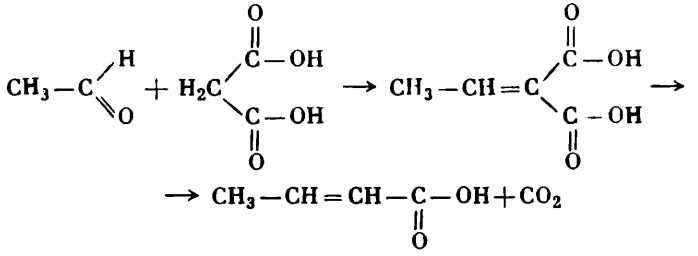
$$CH_2=CH_2+COCl_2 \xrightarrow{AlCl_3} ClCH_2-CH_2-\underset{\underset{O}{\|}}{C}-Cl \xrightarrow[-HCl]{+H_2O} CH_2=CH-\underset{\underset{OH}{|}}{C}=O$$

Methacrylic acid is normally synthesized from acetone and hydrocyanic acid:

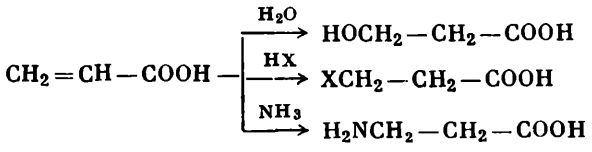


Since not methacrylic acid itself but its methyl ester is finding application, to the mixture of acetone cyanohydrin and sulphuric acid there is added methanol, and methyl methacrylate is directly obtained (from β-hydroxypropionitrile there is also directly prepared methyl acrylate).

Apart from the oxidation of crotonaldehyde, **crotonic acid** can also be obtained by the condensation of acetaldehyde with malonic acid in pyridine solution (Knoevenagel):



Unsaturated acids of the type under consideration behave in certain reactions just like aldehydes and ketones with a conjugated system of bonds. These include the easy addition of water in acid solution, hydrogen halides and ammonia at the olefinic double bond. All these reactions give β-substituted propionic acids, i.e., the reactions proceed contrary to Markovnikov's rule. For example,



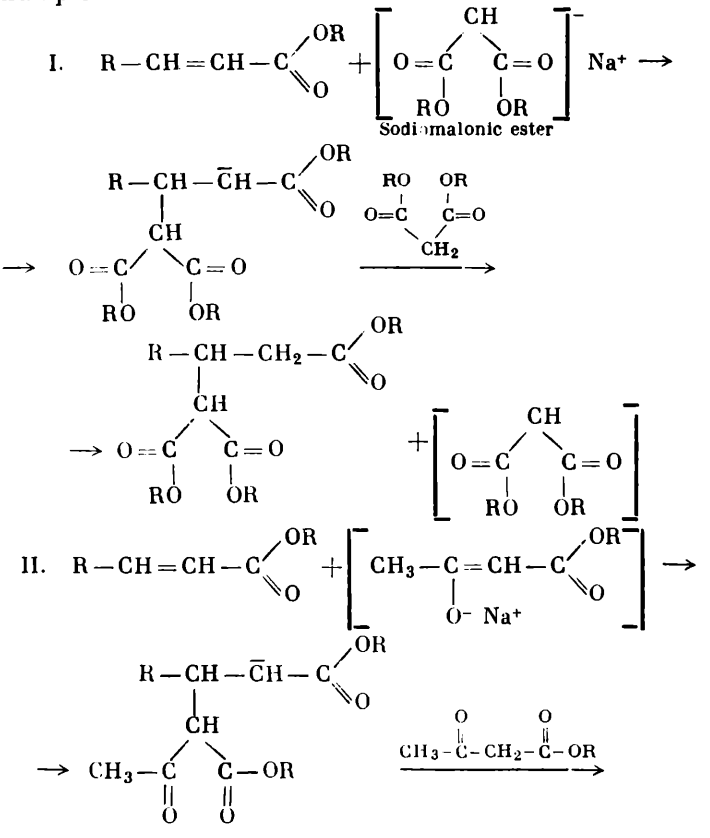
There is no direct evidence that these reactions proceed as a 1,4-addition reaction, but it is quite likely that this is essentially correct, as indicated in Sec. VIII (see page 419).

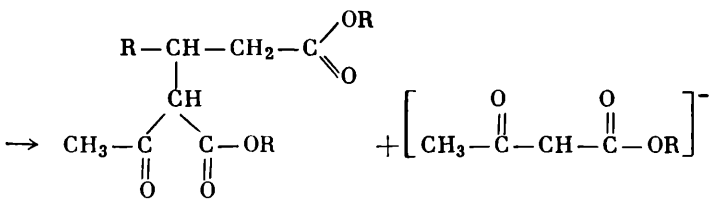
Since the carboxyl carbonyl does not add on hydrocyanic acid, bisulphite, etc., it follows that unsaturated acids do not enter into such reactions; no 1,4-addition of a Grignard reagent to esters of acids are observed either.

The absence of a direct proof of 1,4-addition to α,β-unsaturated acids permits one to regard the addition of water, ammonia and a hydrogen halide as an anti-Markovnikov 1,2-addition across the olefinic bond. In any event the reaction begins with the nucleophilic attack of the anion at one of the carbons of an electron-deficient bond, namely, at the β-carbon atom.

A synthetically important reaction is the Michael reaction (page 401), a particular case of which is the addition, in a strongly alkaline solution, of acetoacetic and malonic esters, acetylacetone or similar compounds to α,β-unsaturated acids and their derivatives.

This reaction consists in the following: the anions (mesomeric) of these compounds exert a nucleophilic attack on the electron-deficient double bond of α,β-unsaturated acids (and also of carbonyl compounds) with the anti-Markovnikov orientation of the attacking anion. The reaction ends with the expulsion of a proton from a new molecule by the transiently formed anion (adduct). The following are examples:

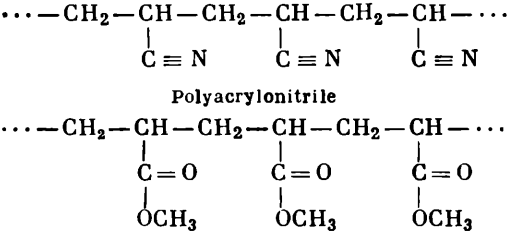




The reactions of α,β-unsaturated acids as dienophiles (the Diels-Alder reaction) with dienes has been discussed in the description of dienes. α,β-Unsaturated acids give an ordinary series of functional derivatives. Acids and their derivatives of the type $CH_2=CR-$ —COOH polymerize readily by a homolytic mechanism (initiators are peroxides and other compounds capable of generating free radicals). The methyl esters of acrylic and methacrylic acids find wide practical application since they form colourless, transparent plastics (polymethylacrylate and polymethyl methacrylate), e.g., Plexiglas which becomes soft at about 100°C and can be reshaped.

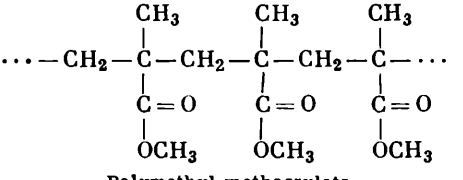
Still more important are the polymers of acrylonitrile, which are utilized for the manufacture of chemical fibres (Orlon, Nitron) which are the best substitutes for wool, and also the copolymers of acrylonitrile and butadiene, from which petrol-resistant synthetic rubbers are produced (Buna N or Perbunan).

Like all "vinyl polymers", the polymers of acrylates and acrylonitrile have a structure of the type:



Polyacrylonitrile

Polymethyl acrylate



Polymethyl methacrylate
(Plexiglas)

Special mention should be made of the properties of acrylonitrile which are important to synthetic chemistry. It can add, in alkaline solution at the double C=C bond, numerous compounds contain-

ing a mobile (replaceable) hydrogen atom, including C—H groups capable of giving up a proton. For example,

$$CH_3-\underset{\underset{O}{\|}}{C}-CH_3+CH_2=CH-C\equiv N \longrightarrow CH_3-\underset{\underset{O}{\|}}{C}-CH_2-CH_2-CH_2-C\equiv N$$

As a matter of fact, the attack is effected by the anion of the reagent on the β-carbon atom of acrylonitrile. This is not restricted to the union with one molecule of acrylonitrile. All the α-hydrogens of aldehydes and ketones can be replaced by the residue of acrylonitrile. As a result of the reaction, the mobile or active hydrogen in an aldehyde or ketone is replaced by the $-CH_2-CH_2-CN$ group, for which reason the process is called **cyanoethylation.** The reaction is evidently similar to the Michael reaction (page 401).

Acrylonitrile can add readily hydroxyl and amino derivatives:

$$ROH+CH_2=CH-C\equiv N \longrightarrow RO-CH_2-CH_2-C\equiv N$$
$$RNH_2+CH_2=CH-C\equiv N \longrightarrow RNH-CH_2-CH_2-C\equiv N$$

Thus, the bond conjugation in C=C—C≡N has the same effect on the properties of the system as the conjugation in the C=C—C=O system. The cyanoethylation reaction (Bruson) has been thoroughly elaborated by A. P. Terentyev and his pupils.

The simplest representative of unsaturated acids with an isolated double bond is **vinylacetic acid**, $CH_2=CH-CH_2-COOH$, which can be made from allyl-magnesium chloride and carbon dioxide:

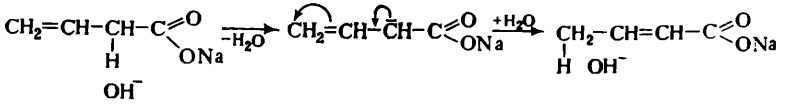
$$CH_2=CH-CH_2MgCl+CO_2 \longrightarrow CH_2=CH-CH_2-\underset{\underset{O}{\|}}{C}-OMgCl$$

When heated with alkali the salts of vinylacetic acid are converted into the salts of crotonic acid:

$$CH_2=CH-CH_2-\underset{\underset{O}{\|}}{C}-ONa \xrightarrow{OH^-} CH_3-CH=CH-\underset{\underset{O}{\|}}{C}-ONa$$

The migration of the double bond under the influence of alkali to the conjugated position is rather widespread and is associated with the low energy level of compounds having a conjugated double bond as compared with their isomers containing an isolated double bond. The mechanism of this bond migration consists in that the base OH^- removes a proton residing in the alpha-position to the carboxyl group

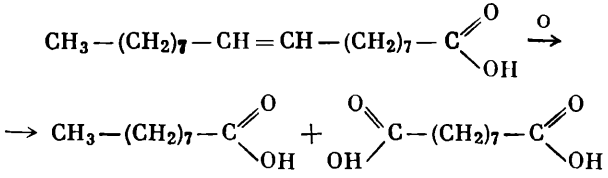
and simultaneously in the allylic position, which renders it easily removable:



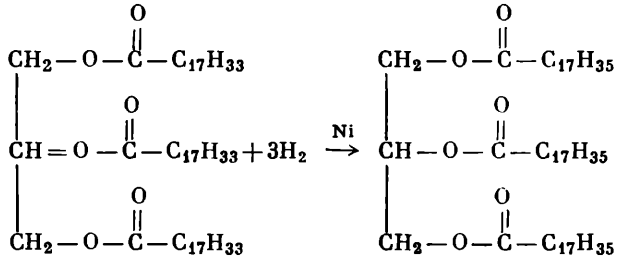
B. Higher Unsaturated Fatty Acids.

Oils and Fats. Lipids

Particularly important are the higher fatty unsaturated acids which are found in ester combination with glycerol in natural fats and oils* (often referred to as "glycerides"). The simplest of these is **oleic acid.** By hydrolysis (saponification) of olive oil it is possible to prepare liquid oleic acid of the composition $C_{17}H_{33}COOH$, which on catalytic hydrogenation (H_2/Ni) absorbs one mole of hydrogen and changes to stearic acid, $C_{17}H_{35}COOH$. From this it is clear that the skeletons of both acids are identical and that there is one double bond in oleic acid. The disposition of this double bond is established by ozonization and oxidation. The oxidation leads to the formation of pelargonic and azelaic acids and proceeds according to the scheme:



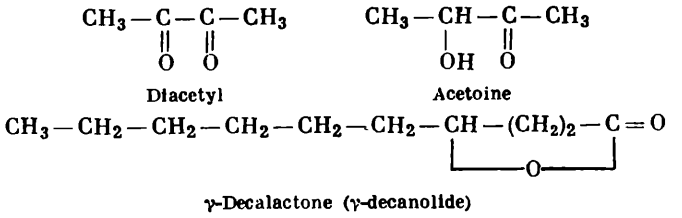
Thus, olive oil, just as many liquid oils, primarily of vegetable origin, contains a liquid glyceride—triolein, which on hydrogenation by hydrogen over a nickel catalyst is converted into solid saturated tristearin:



This process and similar conversions lie at the basis of the *hardening of fats*—the transformation of liquid unsaturated oils of vege-

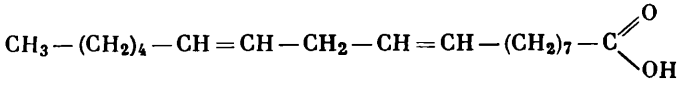
* The fats are solids at room temperature, while the oils are liquids.—*Tr.*

table origin into solid margarine which is churned with skim milk to impart to it the odour of butter; for example,

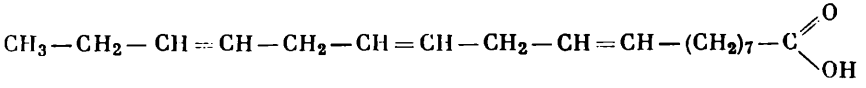


Liquid vegetable oils also contain acids that have a higher degree of unsaturation than oleic acid, for example:

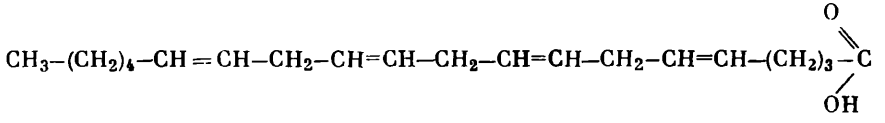
(a) *linoleic acid*



(b) *linolenic acid*



(c) *arachidonic acid*

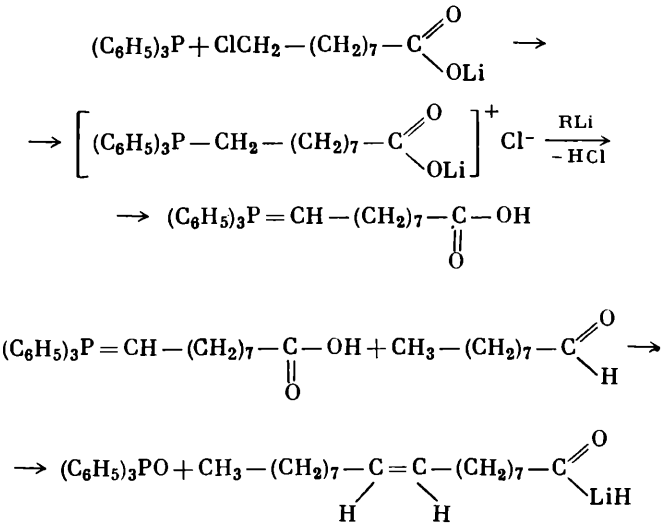


The number of acids contained in vegetable oils amounts to 40, primarily C_{18} to C_{20}, which differ in the number and position of double bonds. They are found as glycerides in linseed, hempseed, sunflower and nut oils and in other, so-called "drying oils".

It has been found in recent years that it is these highly unsaturated acids or the corresponding oils in small amounts, a total of about 5 grams per day, that are necessary to man's life since they have the function of a special vitamin (with the difference that other vitamins are required in a much less amount). The structure of these acids has been established by ozonization. They have also been obtained synthetically.

It is interesting that the Wittig reaction (see Volumes III and IV) can be used to prepare almost pure *cis*-olefins from some ylides of phosphorus (reactive, unstable) and *trans*-olefins from others (slightly reactive, stable). L. D. Bergelson and M. M. Shemyakin have

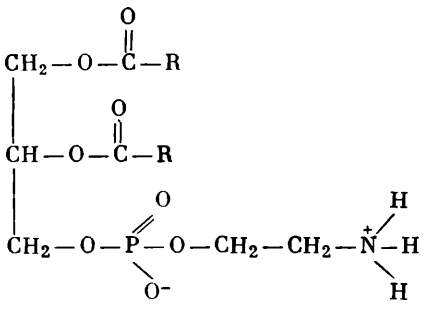
synthesized a number of pure *cis*-unsaturated acids. Below is shown the synthesis of *cis*-oleic acid:



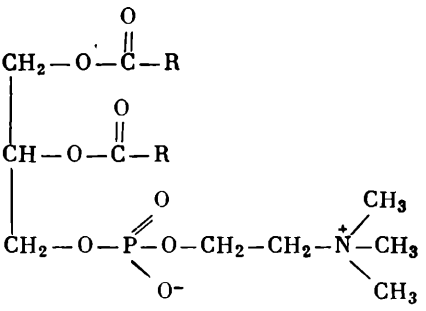
Oils and fats perform the function of valuable foods, the oxidation of which is a source of energy, and play the role of energy reserve, being accumulated in the tissues of the body. Unsaturated acids with the bond system $-CH=CHCH_2-CH=CH-$ cannot be synthesized by the human organism, in contrast to unsaturated oleic acid; they must be supplied ready with food (as vitamins). These acids form the lipids of cell walls and play an important part in rendering these walls semipermeable, as a result of which they hold back some substances and pass others.

Lipids (also known as *lipins* or *lipoids*) are substances contained in the tissues of animals. These compounds are insoluble in water and soluble in organic solvents (hydrocarbons and ether). They include, in particular, the *fats* and waxes, i.e., the full esters of glycerol, and the *phosphatides* or *phospholipids*, i.e., the diglycerides of the fatty acids, in which glycerol has been partially esterified by phosphoric acid and the acid itself esterifies, by its second hydroxyl group, the amino alcohols—choline, $HOCH_2-CH_2-\overset{+}{N}(CH_3)_3$, or ethanolamine, $HOCH_2-CH_2-NH_2$. Below is given the schematic structure of two important phosphatides—**cephalin** (from brain) and **lecithin** (lecithol) contained in many animals and

plants (egg, liver tissue, soybean, etc.):



Cephalin

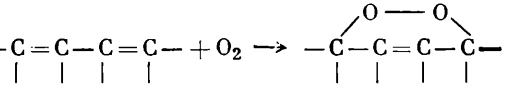


Lecithin

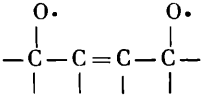
The above-indicated function in the cell walls is performed by the phosphatides with unsaturated acids, particularly with acids containing the divinylmethane grouping $-CH=CH-CH_2-CH=CH-$.

As an example of a thorough investigation into the composition of vegetable oils, we shall mention the work of A. S. Sadykov and N. M. Iskhakov who isolated 13 glycerides from cotton oil, which total 98 per cent of the composition of the oil. Apart from the saturated acids—stearic and palmitic, these glycerides include, in various combinations, oleic and linoleic acids. The principal glycerides of cotton oil are palmito-dilinolein (27 per cent), trilinolein (17 per cent) and palmito-oleo-linolein (17 per cent).

Large quantities of linseed oil are utilized for the manufacture of drying oils and oil-based paints. Drying oils are produced by boiling the oils with a small amount of manganese or lead oxides or the salts of these metals with resin acids (see Volume IV). Processes of two types are involved. First, the isolated double bonds of linoleic and linolenic acids migrate into the conjugated position, and the conjugated double bonds are oxidized by atmospheric oxygen according to the scheme of a sort of diene synthesis:



The resulting peroxide decomposes with the formation of free radicals



which cause the polymerization across the conjugated and isolated C=C bonds. For example, tung oil (from the tung nut), which is used

to make the famous Chinese varnish, contains the glyceride of eleostearic acid, which has three conjugated double bonds; tung oil polymerizes (by the action of the air) more rapidly than linseed oil (from flax seed).

Moreover, the groupings $-CH=CH-CH_2-CH=CH-$, which contain a methylene group in the allylic position, are oxidized by oxygen under the influence of an initiator (a metal ion of high valency) with the formation of hydroperoxides:

$$-CH=CH-CH_2-CH=CH- + M^{3+} \longrightarrow$$

$$\longrightarrow -CH=CH-\dot{C}H-CH=CH- + M^{2+} + H^+$$

$$-CH=CH-\dot{C}H-CH=CH- + O_2 \longrightarrow -CH=CH-\underset{\displaystyle O-O\cdot}{\underset{|}{CH}}-CH=CH-$$

$$-CH=CH-\underset{\displaystyle O-O\cdot}{\underset{|}{CH}}-CH=CH- + -CH=CH-\underset{\displaystyle H}{\underset{|}{CH}}-CH=CH- \longrightarrow$$

$$\longrightarrow -CH=CH-\underset{\displaystyle O-OH}{\underset{|}{CH}}-CH=CH- + -CH=CH-\dot{C}H-CH=CH-, \text{ etc.}$$

The hydroperoxide generates a number of new free radicals, which arise as a result of the abstraction of the allylic hydrogen from another chain or are the products of its decomposition, for example,

$$-CH=CH-\underset{\displaystyle OOH}{\underset{|}{CH}}-CH=CH- \longrightarrow -CH=CH-\underset{\displaystyle O\cdot}{\underset{|}{CH}}-CH=CH- + \cdot OH$$

All these free radicals cause polymerization both at the dienic bonds and at the isolated C=C bonds.

Apart from the polymerization, the cross-linking of the molecules of an unsaturated acid occurs also by reactions of the following type:

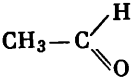
$$\begin{matrix} -CH=CH-\underset{\displaystyle O-O\cdot}{\underset{|}{CH}}-CH=CH- \\ \\ -CH=CH-\dot{C}H-CH=CH- \end{matrix} \longrightarrow \begin{matrix} -CH=CH-\underset{\displaystyle O}{\underset{|}{CH}}-CH=CH- \\ \\ -CH=CH-\underset{\displaystyle O}{\underset{|}{CH}}-CH=CH- \end{matrix}$$

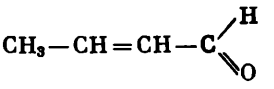
This complicated series of processes result in the hardening of the oil: a tough, durable film is formed; oil-based paints are essentially drying oils with pigments added.

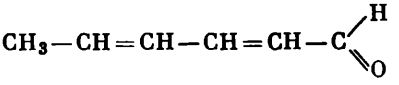
Oleic acid has the *cis*-configuration; its geometrical isomer is solid and more stable elaidic acid. The structures of both acids are identical since they yield absolutely identical products on oxidation; they differ only in the spatial disposition of atoms about the doubly bound carbon atoms (see page 424). Oleic acid is converted into elaidic acid when nitrogen oxide is passed into it.

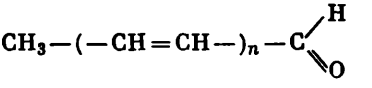
VIII. Vinylogy and the Tautomeric Effect of the Carbon-Carbon Double Bond

A substance which differs from another substance by the presence of a —CH=CH— group (vinyl group) incorporated into its chain is called a **vinylog** of the second compound. For example, a series of aldehydes

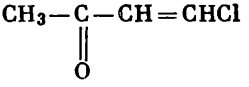




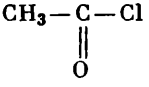




is a series of vinylogs of acetaldehyde and

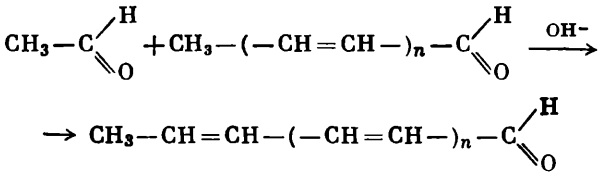


is a vinylog of the compound

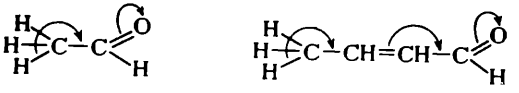


The term vinylog was coined by analogy with homologs which constitute a series of compounds in which the structural formula of each differs from the immediately preceding and following ones by a methylene group (CH_2). The principle of vinylogy, however, is different from that of homology. The point is that the —CH=CH— group and also conjugated systems of n(CH=CH) groups are capable of transmitting the $+T$ and $-T$ effects far along the chain. Therefore the interaction between X and Y united by a chain of —CH=CH— groups into the molecule X—(—CH=CH—)$_n$—Y retains, in a certain degree, the same character as in the case of direct attachment of X to Y (X—Y). Examples of this phenomenon are given on page 368.

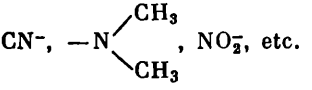
In the series of aldehydes shown above, each member is capable of croton condensation with acetaldehyde due to its end methyl group:



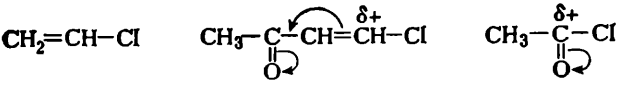
so that the transmission of the $-T$ effect of the aldehyde carbonyl to the carbon of the methyl group is obvious, this effect being of the same character as in the directly joined methyl and carbonyl groups of acetaldehyde:



In chlorovinyl ketones, the chlorine at the vinyl group is completely different from the inactive chlorine of vinyl chloride. It can be replaced by

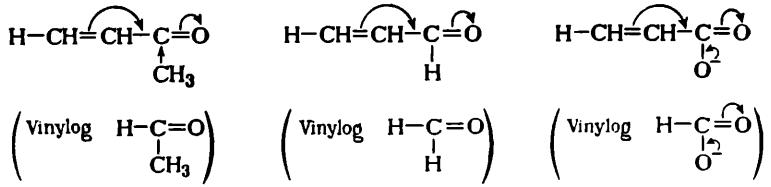


in nucleophilic substitution reactions almost as readily as the chlorine in an acid chloride:

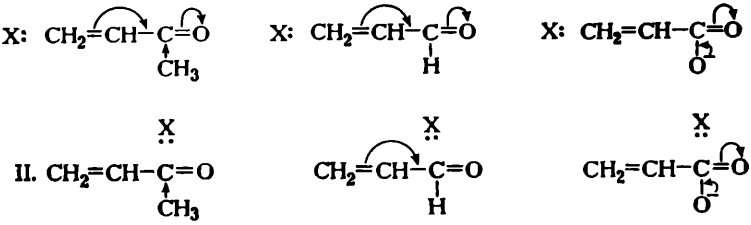


The cause is obvious: the mobility of chlorine in an acid chloride is due to the strong positive charge $\delta+$ on the carbonyl carbon which is thus made accessible to nucleophilic attack by anions and, in general, by any nucleophilic particle. In chlorovinyl ketone the $-T$ effect and its static part—the mesomeric ($-M$) effect—impart a $\delta+$ charge to the chlorine-bearing carbon of the vinyl group. The reaction centre of the carbonyl is transferred to this carbon atom but is suppressed to a certain extent because of the π-electron pair of the —CH=CH— group being shifted to it.

This transfer of reactivity is evidently responsible for the specific properties of unsaturated aldehydes, ketones and acids with a system of conjugated double bonds (C=C—C=O):

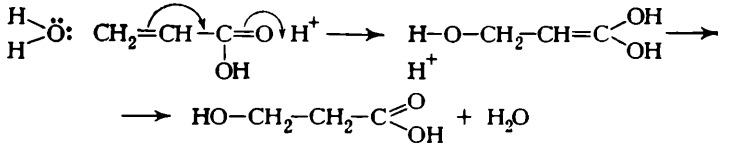


Suppose that the anion X: attacks each of the molecules at the end CH_2 group (I) and, alternatively, at the carbonyl group (II):



If the anion X: attacks the CH_2 group of ketones, the electron pairs of the two conjugated π-bonds are shifted synchronously in the direction of the arrows and the anion becomes attached, without hindrance, to the CH_2 group. But if the attack is directed to the carbonyl carbon, it is interfered with somewhat (as compared with aldehydes) by the $+I$ effect of the methyl group, which supplies electrons and partially compensates for the $\delta+$ charge of the carbonyl carbon. There is no such interference in aldehydes in which the attack is often directed to the carbonyl (for example, the action of a Grignard reagent). When the anion X: attacks an unsaturated acid, the situation is different: the carboxylate anion is found to have lost, almost completely, the ability to conjugate with the CH_2=CH group due to the internal conjugation and the attack either at CH_2 or at the C=O bond does not lead to the addition of X.

In acid medium, certain reagents (H_2O, HCl) successfully attack the CH_2 group of unsaturated acids due to the assistance of hydrogen ion:



C. Dibasic Acids of the Ethylene Series. Maleic and Fumaric Acids

When alcoholic alkali is allowed to react with chlorosuccinic acid, hydrogen halide is eliminated and **fumaric acid** is formed (in the form of a salt):

$$NaO-\overset{\overset{O}{\|}}{C}-CHCl-CH_2-\overset{\overset{O}{\|}}{C}-ONa + C_2H_5ONa \longrightarrow$$

$$\longrightarrow NaO-\overset{\overset{O}{\|}}{C}-CH=CH-\overset{\overset{O}{\|}}{C}-ONa + C_2H_5OH + NaCl$$

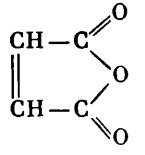
The same acid can be prepared by dehydration of malic (hydroxysuccinic) acid on distillation with the acid:

$$HO-\overset{\overset{O}{\|}}{C}-\underset{\underset{OH}{|}}{CH}-CH_2-\overset{\overset{O}{\|}}{C}-OH \xrightarrow[-H_2O]{H^+} HO-\overset{\overset{O}{\|}}{C}-CH=CH-\overset{\overset{O}{\|}}{C}-OH$$

Fumaric acid occurs in many plants, such as *Fumaria officinalis* (hence its name).

The slow and careful dehydration of malic acid results in the formation of **maleic acid** which is an isomer of fumaric acid. The properties of maleic acid differ sharply from those of fumaric acid, as illustrated by Table 3.6.

The main chemical distinction between these two monounsaturated dibasic acids is the ability of maleic acid to form on heating a cyclic anhydride whose structure can be proved by its hydrogenation into succinic anhydride; fumaric acid cannot be transformed into an anhydride:



Maleic anhydride

Maleic anhydride is a commercial product. It is produced by the air oxidation of benzene in the presence of vanadium pentoxide as a catalyst:

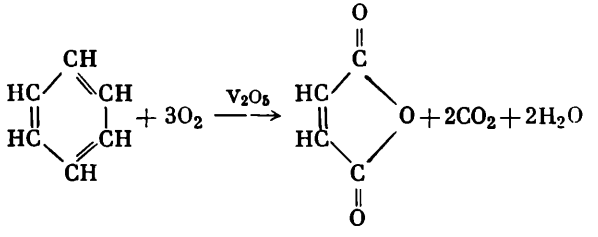
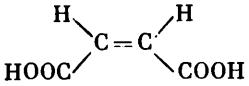
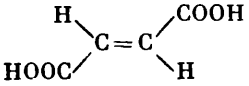


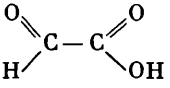
TABLE 3.6. **The Properties of Maleic and Fumaric Acids**

Formula	Name	m.p., °C	b.p., °C	Density d_4^{20}	Dipole moment (in dioxan at 25°C) D	K_{a1}	K_{a2}
	Maleic or *cis*-1,2--ethylenedicarboxylic acid	130	135 (turns into an anhydride)	1.590	2.38	1.7×10^{-2} (at 25°C)	2.6×10^{-7} (at 25°C)
	Fumaric or *trans*--1,2-ethylenedicarboxylic acid	287 * (295)	290	1.635	2.46	9.3×10^{-4} (at 18°C)	2.9×10^{-5} (at 15°C)

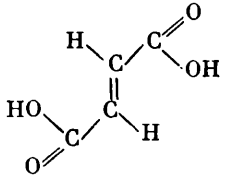
* In a sealed capillary.

IX. Stereochemistry. Geometrical Isomerism II

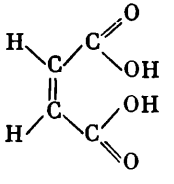
Fumaric and maleic acids give many identical reactions. For example, hydrogen over nickel or platinum hydrogenates both acids to yield succinic acid. Both acids add a water molecule (in the presence of strong acids) to give malic acid. The addition of hydrogen chloride leads in both cases to the same chlorosuccinic acid, and the ozonolysis gives glyoxylic acid:



From this it follows that structurally fumaric and maleic acids are identical, their difference being due to another factor. The fact that it is exactly maleic acid that undergoes cyclization into an anhydride, fumaric acid being incapable of forming a cyclic anhydride, has led to the conclusion that the two carboxyl groups in maleic acid are much closer to each other than the carboxyl groups in fumaric acid and, consequently, the isomerism of these acids is geometrical isomerism (of the *cis-trans* type) and their configurations can be represented as follows:



Fumaric acid



Maleic acid

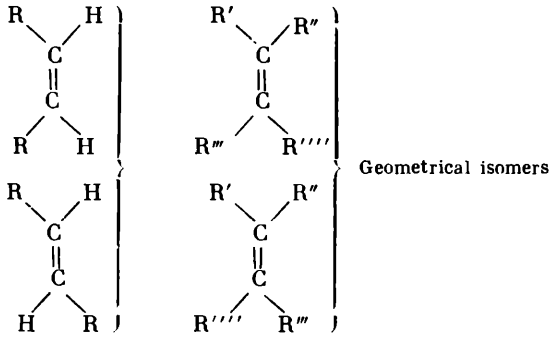
The term **configuration** defines the spatial arrangement of atoms in stereoisomers which differ from one another because their atoms are arranged differently in space. This term is contrasted to such terms as structure (constitution) and conformation (page 425).

The arrangement of identical groups on one side of the double bond and of the carbon atoms is called the *cis*-configuration, as has been said on page 333; if they are arranged on opposite sides, the arrangement is called the *trans*-configuration. Thus, fumaric acid is *trans*-ethylenedicarboxylic acid and maleic acid is its *cis*-isomer.

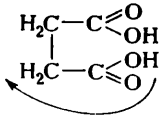
The inference concerning the structures of the two acids is corroborated by the oxidation of benzene to maleic anhydride and not to fumaric acid. The point is that in benzene the two carbon atoms being oxidized to carboxyls are "fixed" in the *cis*-position due to the cyclic structure of benzene. This conclusion is in keeping with the mutual influence of the two carboxyl groups. In this case, one speaks of the so-called **field effect** (an electrostatic effect) transmitted not

along the chain of atoms (the inductive effect is relayed along the saturated chain and the tautomeric or electromeric effect along the unsaturated chain) but directly through space. Naturally, the field effect is stronger in the case of maleic acid because its two carboxyl groups are closer to each other. One carboxyl group being close to the other increases the mobility of the second hydrogen by repulsion (due to the presence of an active hydrogen in it). Therefore the first dissociation constant of maleic acid is greater than that of fumaric acid in which the two carboxyl groups are too far apart to interact directly. After the hydrogen ion has been removed from one carboxyl group the carboxylate anion, on the contrary, begins to attract, due to its negative charge, the hydrogen ion of the second carboxyl group, the attraction being the stronger the closer are the two carboxyl groups to each other. It is for this reason that the second dissociation constant of maleic acid is lower than that of fumaric acid.

Note that succinic acid has no geometrical isomers and it may be said, by way of a generalization, that geometrical isomerism is not characteristic of saturated acyclic compounds and is observed only in the case of compounds with a double carbon-carbon bond:

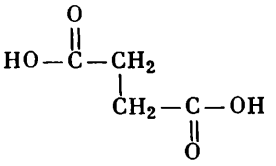


The absence of geometrical isomers can be accounted for by the fact that the rotation about the axis connecting two saturated carbon atoms, say, in succinic acid, is unhindered (from the chemical point



of view), i.e., it requires little energy (2-3 kcal/mole) that can be provided by thermal motion at room temperature and no chemical action is needed. Therefore, identical or equally charged substituents

are found to be as far apart as possible, just as, for example, in succinic acid:



which does not prevent the formation of a cyclic anhydride by succinic acid (free rotation).

Any arrangement of atoms in a molecule, which depends on the rotation about the axis connecting the saturated atoms (a pair or a chain of atoms) is called the **conformation**. Different conformations of one and the same molecule are not different isomers since they are readily converted into one another.

As an example, Fig. 3.1 presents the various conformations of succinic acid in a projection (Newman projection); the C—C axis is perpendicular to the plane of the paper.

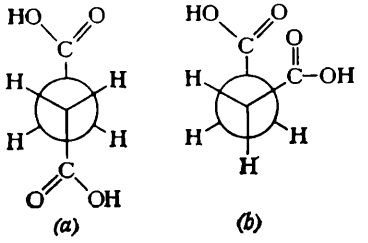


Fig. 3.1.

Conformations of succinic acid:

(*a*) *trans* conformation; (*b*) *skew* (or *gauche*) conformation. Only the *trans* conformation is stable.

In contrast to saturated carbon atoms, for olefinic carbon atoms (doubly bound) the rotation about the connecting axis requires a considerable amount of energy, of the same order as in ordinary chemical transformations. Therefore, the conformation is fixed in this case into a configuration, as a result of which geometrical (or *cis-trans*) isomerism is observed.

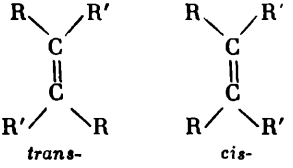
We have already encountered the phenomenon of geometrical isomerism which is a particular case of stereoisomerism, in the discussion of *cis-* and *trans*-1,2-dichloroethylenes, oleic and elaidic acids.

We may add crotonic acid (*trans*-isomer) and isocrotonic acid (*cis*-isomer).

It should be noted (for more detail, see Vol. II) that the *cis-trans* isomerism is also typical of cyclic compounds in which the presence of a ring hampers the interconversion of *cis*- and *trans*-isomers; for example,

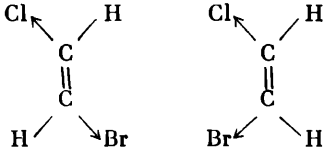
From the comparison of the physical properties of the *cis*- and *trans*-isomers of fumaric and maleic acids (see Table 3.6) it is seen that the difference in the properties of geometrical isomers is no less than in the case of structural isomers. Special mention should be made of the difference in the dipole moments of the *cis*- and *trans*-isomers, which serves as one of the main criteria for elucidation of their configurations.

For example, in the case of substituted ethylenes of the type



the dipole moment of the *trans*-isomer is zero since it is obtained by the vectorial addition of the constituent bond dipole moments which are naturally oriented in pairs in opposite directions (at an angle of 180°) and, when added up, give zero. A *cis*-compound has a dipole moment different from zero.

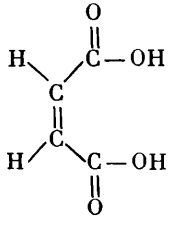
If the substituents are not identical, the configuration can nevertheless be determined by comparing the values of the dipole moments. For example, though the dipole moment of *trans*-chlorobromoethylene is different from zero, it will of course be smaller than the dipole moment of *cis*-chlorobromoethylene:



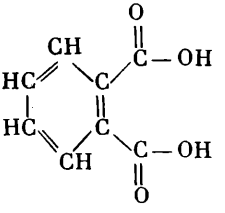
since in the vector addition the moments of the C—Cl and C—Br bonds in the *trans*-compound, which are at an angle of 180° to each other, will subtract and give a relatively small difference, whereas in the *cis*-isomer they are directed at an angle of 120° and the diagonal of a parallelogram, whose sides are equal to the dipole moments of the C—Cl and C—Br bonds, will be a value close to the mean of the sides of the parallelogram and will be greater than the difference between them.

The dipole moments of molecules were first measured by Debye in the twenties of this century. Before that time the inferences concerning *cis*- and *trans*-configurations had been based on considerations such as those given above in the discussion of the configurations of fumaric and maleic acids, i.e., primarily the ability of *cis*-isomers to undergo cyclization or their formation on disclosure of the ring. Such chemical transformations must not disturb the bonds between the substituents and olefinic carbon atoms since this often leads to a change of the configuration. In the case of fumaric and maleic acids this requirement is satisfied. Of course this criterion is not applicable to any pair of geometrical isomers. For instance, it can by no means be applied to dichloroethylene because it is impossible to obtain cyclic derivatives from it without disturbing the C—Cl bonds, and dichloroethylene itself cannot be prepared from the ring without rupture of the bonds with olefinic carbon atoms. In such cases, one can judge, with a certain degree of probability, about the configuration by analogy with any known compound from a comparison of their physical constants. If, for example, the configurations of both dichloroethylenes are known and those of both dibromoethylenes are unknown, then it is obvious that the configurations of dibromoethylenes can be deduced with certainty by comparing the boiling points of the four compounds (see Table 3.4, page 382).

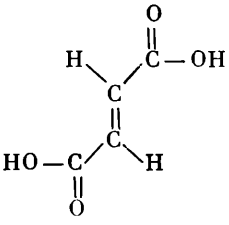
For this purpose, use may be made of the more remote analogy, as was done by Werner (*Werner rule*). The point is that, as seen from their formulas, *ortho*-disubstituted benzene derivatives exhibit a certain geometrical analogy with *cis*-isomers, and *para*-substituted ones with *trans*-isomers (for *ortho*- and *para*-isomers, see Volume III, "Benzene and Its Structure"):



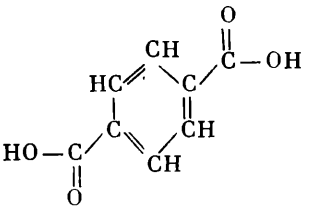
m.p. 130° C



m.p. 131 °C



m.p. 287° C



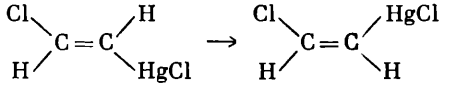
sublimes above 300° C

If, for instance, the *ortho*-compound is a lower-melting isomer and the *para*-compound has a higher melting point, it follows that the *cis*-isomer, which is geometrically close to the former will have a lower melting point than the *trans*-isomer.

Of course, such a comparison could be made with the use of other constants as well, say, the dissociation constants K_{a1} and K_{a2} of all the four acids in the example given above.

Just as any analogy, Werner's rule should be used with caution.

The *cis*- and *trans*-isomers differ also in energy content: in the case of similar or identical substituents (which electrostatically repel one another) the more stable (i.e., lower in the energy level) is the *trans*-isomer. *cis-trans*-Isomers are capable of interconversion (stereomutation). Energetically richer compounds (often, *cis*-isomers) pass into their geometrical isomers under the action of free radicals and, occasionally, of electrophilic reagents. For example, oleic acid is converted to elaidic acid when acted on by NO which has an unpaired electron. Traces of iodine or nitrogen oxides turn maleic acid into fumaric acid. *trans*-β-Chlorovinyl mercurichloride can be transformed into the more stable *cis*-isomer by the action of peroxides (which are capable of generating free radicals):

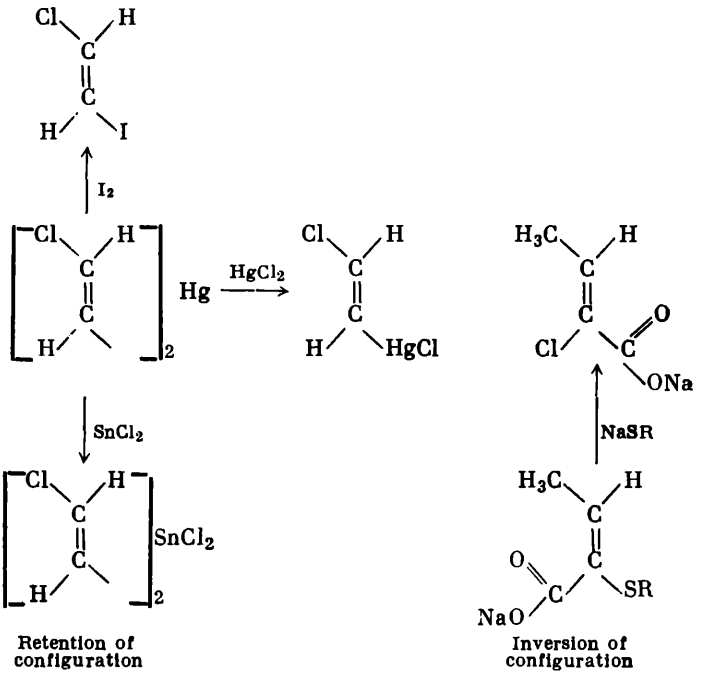


trans- *cis-*

The conversion of a more stable geometrical isomer into a less stable one requires energy and is therefore often accomplished by the action of ultra-violet light. In this way, fumaric acid can be converted to maleic acid.

In substitution reactions involving the replacement of an atom or group attached to the olefinic carbon atom, the following regularities have been observed (A. N. Nesmeyanov, A. E. Borisov). Electrophilic and homolytic substitutions (reactions of the second order are meant here) always proceed with retention of configuration. Nucleophilic substitution inverts the configuration often but not

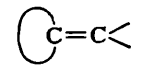
invariably. The following are examples:



X. Physical Methods of Determination of the Structure of Organic Molecules I

The entire science of organic chemistry is devoted to the elucidation of the structures of organic compounds and their synthesis based on the knowledge of structures and typical reactions of formation of the various bonds. We already know how the structure of an organic compound can be determined by chemical methods which remain to be the principal methods but are more and more supplemented and often replaced by physical methods. The specificity of chemical methods of structure elucidation can briefly be formulated as follows: these methods serve to establish close relations in a series of compounds (compounds of related structure) and to elucidate the structure of one or more key compounds of this series by means of their gradual **destruction** (or, as it is often called, **degradation**). This chemical method allows us to determine the structure of any compound, no matter how complex it is, but it requires a considerable amount of work. This is increasingly facilitated by new physical methods of separating and identifying degradation products, parti-

cularly by chromatographic techniques (page 50). A method which is a combination of the degradation method and the identification of molecular fragments (by their molecular weight) is mass spectrometry (see Volume II). The diverse, constantly developing physical methods provide a means of ascertaining important structural details, such as the nature of bonds, interatomic distances and angles, the presence or absence of interactions between electron orbitals (e.g., conjugation), the presence or absence of unpaired electrons (i.e., the presence of an uncompensated spin). The nuclear magnetic resonance (NMR) technique (see Volume II) can be used to determine, for atoms having a nuclear magnetic moment (hydrogen), the presence in a molecule and the number of differently bound hydrogen atoms such as those in hydroxyl, methyl, methylene and methine groups, and *cis*- and *trans*-arranged hydrogen atoms. There are methods which reveal other structural details—the presence of double and triple bonds and their nature (whether they are endocyclic, semicyclic, i.e., contiguous to one of the carbon atoms in the ring, exocyclic, conjugated, etc.).



Many of the existing methods enable one to elucidate, rapidly and with certainty, the configuration of a compound, which can also be done by chemical means, or to get an idea of the conformation, which is almost impossible to do with the aid of chemical methods. Only X-ray diffraction analysis (see page 444 *et seq.*) seems to be capable of providing a detailed elucidation of the structure and, hence, of replacing a chemical study. But, in actual fact, this method cannot yet be used alone for the purpose because, first, it is limited to crystalline substances with well-developed crystals; second, it is incapable of determining the position of hydrogen, and third, is unusually cumbersome, especially in calculations.

A knowledge of the potentialities of each of the physical methods and work in contact with physicists becomes more and more indispensable to an organic chemist. Since physical methods of investigation of substances are expounded in courses of physics and physical chemistry, we shall give but a very brief outline of these methods—only from the viewpoint of their use by an organic chemist.

(A) Heats of Formation of Compounds and Bond Formation Energy

These important quantities are measured by thermochemical methods. The measurements are based on Hess's law (1840). If a system may pass from state I into state II by two different paths through

the various transition states, then at constant volume or constant pressure the sum of the heat effects for the first path is the same as that for the second. The difference in the heat effects of the two processes can be found as follows. The compound under study is subjected to a chemical transformation (for example, the complete combustion with oxygen in the Berthelot bomb); the heat evolved in this reaction is determined. Then the elements, all in their standard states*, are converted into the same products (by combustion in the case under consideration) and the heat of this conversion is determined. According to Hess's law, the difference found is the heat of formation of a given compound from its elements, all in their standard states.

The heat effect of a reaction at constant volume

$$Q_V = U_1 - U_2$$

is equal to the decrease in the internal energy of the system.

The heat effect at constant pressure

$$Q_P = H_1 - H_2$$

is equal to the decrease in the enthalpy of the system.

The two heat effects are related as follows:

$$Q_P = Q_V - P\Delta V$$

The term $P\Delta V$, i.e., the product of the pressure by the change of volume, is practically equal to zero for a condensed phase (a liquid and a solid) and $Q_P = Q_V$. But for gases the difference between Q_P and Q_V is considerable.

It should be noted that the standard state of the elements is chosen purely arbitrarily. For example, graphite with its complex structure and with a carbon atom in the second valence state is chosen as the standard state of carbon, and the pure gas (at 25° C and 1 kg/cm²) with diatomic molecules is chosen for hydrogen, oxygen and nitrogen. Thus, when a compound is being formed from its elements, the bonds are not only made but also broken. Therefore, the calculation of the heat of formation from the free atoms of elements is more spectacular in terms of the gaseous state at 25°C and 1 kg/cm². For this purpose, to the heat of combustion of the elements in their standard states must be added the heats of formation of free atoms from elements (for the standard states of both), which are equal to the following values (in kcal/g-atom):

C	170	F	19
H	51.7	Cl	28.5
O	58.6	Br	22.7
N	112.6	I	17.2

* The standard state is defined as an allotropic modification of an element and a state of aggregation, which is stable under normal or standard conditions (25 °C and 1 kg/cm²).

The heats of combustion of elements are: 94.05 kcal/g-atom for carbon and 34.16 kcal/g-atom for hydrogen (to liquid water).

The most widely used method of combustion has a substantial drawback: the heat of formation is calculated as the difference in the heats of combustion between the substance and the elements. This difference is not great as compared with both constituent heats, and therefore the accuracy of determination of the heat of formation is lowered because of all experimental errors. For more accurate determinations (but in more special cases), use is made, for example, of the heats of catalytic hydrogenation of olefinic bonds.

The heats of formation of compounds from atoms (or from their elements) in their standard states can be used to calculate the heats of formation of single, double and triple bonds for the various elements (see Table 3.7). The calculation is based on the assumption of the additivity of the heat of formation of a compound, which is made up of the heats of formation of all its bonds. Departures from

TABLE 3.7. **The Energies of Chemical Bonds** *

Bond	Energy, kcal/mole	Bond	Energy, kcal/mole
C—H		C=N	147
in alkanes	98.7	C≡N	212.6
in alkenes	99.4	O—H	110.6
in alkynes	96.3	N—H	93.4
in benzene	100.7	N=O in nitro compounds	45
C—C		N—N	39
in alkanes	82.6	N=N	100
in benzene	116.4	N≡N	225.8
C=C in alkenes	145.8	C—F	116
C≡C in alkynes	199.6	C—Cl	81
C—O	85.5	C—Br in bromoalkanes	68
C=O		C—I in iodoalkanes	51
in formaldehyde	166	F—F	36.6
in other aldehydes	176	Cl—Cl	58.0
in ketones	179	Br—Br	46.1
in CO_2	192.0	I—I	36.1
C≡O in carbon monoxide	255.8	C—S	65
C—N	72.8	S—H	83
		O—O	35

* The data are taken from: L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, N.Y., 3rd ed., 1960; F.D. Rossini, et al., *Selected Values of Chemical Thermodynamic Properties*, Circular of the National Bureau of Standards, Washington, 1952.

additivity are encountered, for example, in bond conjugation and are called the resonance or conjugation energy. Such a deviation, say, for 1,3-butadiene is 3.5 kcal/mole, and for benzene, 39 kcal/mole (i.e., the value found additively from the heats of bond formation is greater, by the value of resonance energy, than that determined experimentally).

One should clearly realize that the bond-making (or bond-breaking) energies thus obtained are the average values. The energy of detachment, say, of the first hydrogen atom from the molecule of an even symmetrically built hydrocarbon—methane or ethane—is always lower than the energy required to detach the second hydrogen atom, etc. The energy of the C—H bond decreases in the following order: primary carbon-hydrogen; secondary carbon-hydrogen; tertiary carbon-hydrogen, etc.

The true bond-making (or bond-breaking) energies are dissociation energies. They can be determined, in particular, kinetically, by measuring the rate of dissociation of a molecule at various temperatures. For example,

$$CH_4 \rightleftarrows CH_3\cdot + H\cdot$$

Since the activation energy of the reverse reaction—the formation of a molecule from free radicals—is equal to zero, the activation energy of the dissociation reaction is exactly equal to the heat required to break a bond. The dissociation energies obtained in this way or by other methods are generally in good agreement with the values determined thermochemically.

(B) The Electronegativity Scale

The energies of formation of bonds between atoms in their standard states can be used, according to Pauling, to calculate the relative electronegativities of the elements.

Let us designate the experimentally determined energy of bond formation for two identical atoms, say, the energy of the C—C bond, by E_{CC}, and the energy of the C—H bond, by E_{CH}. Then the geometric mean of these values will be $\sqrt{E_{CC}E_{CH}}$. Let Δ' denote the deviation of the experimentally found energy of the C—H bond from the geometric mean. Then

$$\Delta' = E_{CH} - \sqrt{E_{CC}E_{CH}} \tag{1}$$

$$X_C - X_H = \frac{\sqrt{E_{CC}E_{CH}}}{\sqrt{\Delta'}} \tag{2}$$

Relation (2) serves as an energy measure of the deviation of the real C—H bond from the ideal homopolar C—H bond, i.e., as a characteristic of the difference in the electronegativities of atoms C and

H, designated as X_C and X_H. With normal differences in bond energies, amounting to several tens of calories, the geometric mean differs little from the arithmetic mean, and almost the same result is obtained when use is made of the ratio of the arithmetic mean to the deviation of the true energy from it.

Having performed the above procedure for a number of bonds between atoms A and B, we can find the electronegativity differences $X_A - X_B$, from which it is not difficult to determine the electronegativity values X_A and X_B. In carrying out the entire calculation, instead of the quantity Δ', Pauling made use of $0.18\Delta'$, which is nothing more than $\sqrt{\Delta'/30}$, i.e., he expressed Δ' in values equal to 30 kcal/mole. Besides, to each value of electronegativity thus obtained he added 2.05, i.e., he changed the reference value by this number in order to render the entire electronegativity scale positive. It is the differences in electronegativities that count. In this way the following electronegativity scale was obtained:

K	0.8	B	2.0	Br	2.8
Na	0.9	H	2.1	N	3.0
Li	1.0	P	2.1	Cl	3.0
Ca	1.0	C	2.5	O	3.5
Mg	1.2	S	2.5	F	4.0
Be	1.5	I	2.5		

The electronegativity of elements in compounds should not be confused either with the electrode potential, which depends on the free-energy difference between an element in its standard state and its ionic solution, or with electron affinity (or with the ionization potential).

The partially polar covalent bond between two atoms, A and B, having different electronegativities is expressed by Pauling in terms of resonance as a superposition of a purely covalent and a purely ionic structure, in which the electronegativity of B is higher than that of A:

$$A : B \leftrightarrow A^+B^-$$

The wave function of this molecule, A—B, can be represented as follows:

$$\psi_{AB} = a\psi_{A:B} + b\psi_{A^+B^-}$$

(the localized-pair method).

(C) The Dipole Moments of Molecules

A molecule is built up of positive atomic nuclei and electrons distributed in space. In a general case, the centres of "gravity" of positive nuclear charges (totalling $+e$) and negative electronic charges ($-e$) do not coincide and are separated by a distance l. The **dipole**

moment μ of the molecule is then equal to el and is a vector quantity. If e is measured in absolute electrostatic units (one fundamental electronic charge is equal to 5.1×10^{-10} esu) and l in angstrom units (10^{-8} cm), then the dipole moment will be expressed in Debye units: one Debye unit is (1 D) $= 10^{-18}$ esu.

Naturally, the dipole moment is an important characteristic of a molecule. Only for molecules having a centre of symmetry, such as CH_4, C_2H_6, CCl_4, C_6H_6, the centres of the positive charge ($+e$) and negative charge ($-e$) coincide and the distance l, and hence the dipole moment μ, is equal to zero. For each of the atoms making up a molecule the inner electrons (i.e., those which do not participate in valency bonds) have a "centre of gravity" in the centre of the atom with its positive charge. Hence, the manifestation of the net dipole moment of the molecule must be affected only by the net (residual) positive charges of the atoms and the negative charges of the bonding electrons. The bonding electrons are largely concentrated on more electronegative atoms.

The dipole moment of a molecule may be regarded as a vector sum of the dipole moments of its individual bonds. The dipole moments of the bonds can be calculated if one knows the dipole moment (for its experimental measurement, see below) and exact geometry of the molecule (the angles between the valence directions, the interatomic distances). Thus, from the dipole moment of water (in the gaseous state) equal to 1.84 D and the angle

equal to 104°, the dipole moment of the O—H bond is calculated as the length of one side of a parallelogram, the angles of which are

TABLE 3.8. **The Dipole Moments of Bonds in the Saturated Series, in Debye Units (D)**

Bond	μ	Bond	μ	Bond	μ
C—C	0	C=O	3.2	H—O	1.51
C—H	0.4	C—F	2.3	H—S	0.68
C—N	1.20	C—Cl	2.3	H—Cl	1.08
C=N	1.25	C—Br	2.2	H—Br	0.78
C≡N	4.0	C—I	2.0	H—I	0.38
C—O	1.6	H—N	1.31		

104° and 76° and the minor diagonal is 1.84:

$$\mu_{OH} = \frac{1.84}{2 \sin 76^\circ} = 1.50\text{D}$$

Table 3.8 lists the dipole moments of the bonds typical of organic compounds.

The dipole moment of a molecule, more precisely the absolute value of this vector quantity, is determined by measuring the dielectric constant of the substance in the gaseous state or in solution in a non-polar solvent and by using the Clausius-Mosotti-Debye equation:

$$P = \frac{\varepsilon - 1}{\varepsilon + 2} \frac{M}{d} = \frac{4\pi}{3} N_0 \left(\alpha + \frac{\mu^2}{3kT}\right) \tag{1}$$

where P = total molar polarization of the substance in the gaseous state
ε = its dielectric constant
M = molecular weight
d = density
N_0 = Avogadro number (the number of molecules in a gram-molecule, equal to 6.023×10^{23})
α = molecular polarizability of the molecule, equal to the value of dipole moment induced in the molecule by unit electric field
k = Boltzmann's constant
T = absolute temperature, °K
μ = dipole moment, in Debye units (the constant R from the equation $PV = RT$ as applied to a single molecule is equal to 1.38×10^{-16}).

The unknown quantities on the right-hand side of Eq. (1) are μ and α (it is assumed that ε has been measured*). Eliminating α, the dipole moment μ can be determined.

There are two ways for elimination of α. One way is to measure P $\left(\text{i.e., } \frac{\varepsilon - 1}{\varepsilon - 2} \frac{M}{d}\right)$ at a series of temperatures and to plot its values along the ordinate and the values of $1/T$ along the abscissa. Since the relation is of the type

$$P = a + \frac{b}{T} \tag{2}$$

(α is practically independent of temperature), it will be expressed graphically by a straight line with a slope equal to b. The value of b,

* As known, if the potential difference across a parallel-plate condenser is measured (at the same charge) with the material between the plates having a dielectric constant ε and in vacuum, the value obtained in the first case will be lower than that in the second by a factor of ε.

which is not difficult to calculate by comparing Eqs. (1) and (2), is given by

$$b = \frac{4\pi}{9} \cdot \frac{N_0}{k} \mu^2$$

Substituting the numerical values of π, N_0 and k, we find the value of the dipole moment in Debye units:

$$\mu = 0.0127 \sqrt{b}$$

An alternative way is as follows. It is known that molar refraction R (see page 441) is a measure of molecular polarizability and is given by the Lorenz-Lorentz formula:

$$R = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d}$$

where n = refractive index for the specified wavelength, usually for sodium D line
M = molecular weight
d = density at a given temperature.

When placed in an alternating electromagnetic field at the frequency of visible light molecules have no chance for their dipoles to be oriented in the direction of the field. The alternating field affects only the shift of electrons in accordance with their polarization, a measure of which is just the molecular refraction (or refractivity) R. The value of R, however, must be extrapolated for an infinite wavelength (i.e., for the same field in which the value of P has been measured), which can be done with the aid of the simple dispersion formula. The values obtained are 3-4 per cent lower than R for the sodium D line.

We rewrite Eq. (1) in the following form:

$$P = \frac{4\pi}{3} N_0 \alpha + \frac{4\pi}{3} N_0 \frac{\mu^2}{3kT}$$

and subtract R_∞ from both sides of the equation:

$$P - R_\infty = \frac{4\pi}{3} N_0 \frac{\mu^2}{3kT}$$

Now the right-hand side does not contain the polarizability term α and the only unknown quantity is the dipole moment, which is calculated from the formula

$$\mu = 0.0127 \sqrt{(P - R)\,T}$$

Thus, the measurement is performed at a single specified temperature and the values of ε, n and d are measured for a given substance with a molecular weight M.

Such are measurements of the dipole moment μ for gases. For a mixture of two liquids the molar polarization is given by

$$P_{1,2} = C_1P_1 + C_2P_2 = \frac{\varepsilon - 1}{\varepsilon + 2} \cdot \frac{C_1M_1 + C_2M_2}{d}$$

whence

$$P_2 = \frac{P_{1,2} - P_1}{C_2} + P_1$$

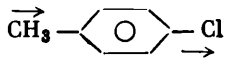
Here P_1 and P_2 are the molar polarizations of the components; C_1 and C_2 are their molar fractions in the mixture; M_1 and M_2 are their molecular weights.

The dipole moment of a substance of interest is measured in a nonpolar solvent (having a zero dipole moment), say, in C_6H_6, C_6H_{14}, CCl_4, etc., at several concentrations, for example, at C_2 ranging from 0.001 to 0.01 or from 0.02 to 0.10, depending on solubility, accuracy of determination and the value of P_2. In most cases, the P_1 value of the solvent depends to a certain extent on P_2 and one has to extrapolate to $C_2 \to 0$. For this to be done, the values of P_2 obtained are plotted along the ordinate and the corresponding values of C_2 along the abscissa, and the ordinate value is found at $C_2 \to 0$, i.e., upon intersection of the curve with the ordinate.

Ordinarily, the values of μ in solution differ little from those in a gas.

Certain fields of application of dipole moments in chemistry. *Structure.* Saturated hydrocarbons of even unsymmetrical structure have a dipole moment equal or very close to zero. The same applies to the simplest purely aromatic structures, such as benzene, naphthalene, anthracene. A combination of the aliphatic methyl group with the benzene ring (toluene, $C_6H_5CH_3$), however, gives a small dipole moment ($\mu = 0.34$).

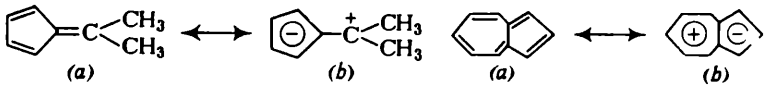
From a comparison of the dipole moment of chlorobenzene (1.55), in which the negative end of the dipole is on the chlorine atom, with the dipole moment of *n*-chlorotoluene (1.95)



n-Chlorotoluene

it is clear that the dipole moments induced by the methyl group and chlorine are summed up and hence have the same direction in space, from which the direction of the dipole of the methyl group of toluene is deduced.

There are hydrocarbons with a considerable dipole moment, say, fulvenes and azulene:



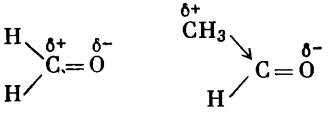
Dimethylfulvene ($\mu = 1.48\,D$) Azulene ($\mu = 1\,D$)

Their dipole moments are caused by a certain charge separation due to the capture of an electron by the five-membered ring, which becomes aromatic as a result. In azulene, the seven-membered ring, which has lost an electron, also becomes aromatic (see Volume IV). The low value of dipole moment means, however, that in both compounds the resonating structure (b) with the completely separated charge is far from being achieved.

In the series of monofunctional aliphatic compounds the dipole moments remain practically constant within a homologous series. This is evidence that the dipole moment is completely concentrated in a functional group. For example,

Alkyl fluorides and iodides	1.9	Alcohols	1.65
Alkyl chlorides and bromides	2	Aldehydes and ketones	2.72
		Nitriles	4.05

Certain deviations are observed only for the first members of the homologous series. For instance, the dipole moment of formaldehyde (2.27) is much lower than that of acetaldehyde (2.72). This is a consequence of the inductive $+I$ effect of the methyl group, i.e., more electrons are "supplied" by the methyl group than by hydrogen (the effect that was shown for toluene):



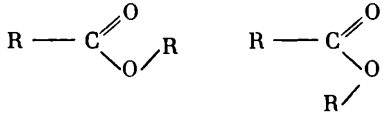
In going to alkenes substituted at an unsaturated carbon atom or aromatic monofunctional compounds typical deviations are observed from the values given above for saturated compounds. For example, the dipole moment of vinyl chloride is 1.44 and that of chlorobenzene 1.57 (compare with 1.86 for methyl chloride and 2 for ethyl chloride). Below are given the dipole moments (in Debye units) of saturated and aromatic compounds:

$AlkOCH_3$	1.22	$AlkNO_2$	3.68	ArCHO	2.76
AlkOH	1.65	AlkCN	4.05	$ArCOCH_3$	3.0
AlkCOOH	1.68	$ArOCH_3$	1.48	$ArNO_2$	4.21
AlkCHO	2.72	ArOH	1.4	ArCN	4.39
$AlkCOCH_3$	2.78	ArCOOH	1.73		

Configuration. The measurement of dipole moments, as has already been said, enables one to identify centrosymmetrical molecules by their zero dipole moment. For instance, it is possible to differentiate between the *cis*- and *trans*-configurations of olefinic compounds. If the substituent groups are different, even in this case, by comparing the dipole moments of the *cis*- and *trans*-compounds, one can differentiate these configurations.

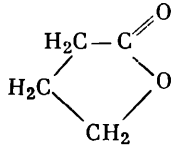
This is also possible for *cis*- and *trans*-arrangements of substituents in the 1,4-positions of cyclohexane in spite of the fact that its molecule is not flat and the rotation in the ring is not completely eliminated. Nevertheless, for the *cis*-derivative (of course, in case the substituents are identical) the dipole moment is higher than for the *trans*-isomer.

Conformation. An example of elucidation of the conformation of a molecule is the consideration of the dipole moment of an ester, for which two extreme conformations are possible:



I II

The esters of the homologues of acetic acid have a dipole moment of about 1.73, which differs sharply from the dipole moment of butyrolactone (4.12), which is a cyclic inner ester. Its structure can correspond only to conformation II.



Butyrolactone

Therefore, conformation I is preferred for the esters of the homologues of acetic acid.

(D) Molar Refraction

Molecular refraction (or **refractivity**) R is a measure of the polarizability of a molecule under the influence of the alternating electromagnetic field of light, in which only the electrons rearrange themselves, but the permanent dipoles of molecules have no chance to turn and reorient themselves:

$$R = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d}$$

where n is the refractive index of light of a definite wavelength (usually the sodium D line) at a definite temperature; d is the density at the same temperature.

Molar refraction, say, at 20°C, is designated as R_D^{20}. But R depends little on temperature.

The most important fact for the chemist in this respect is that R for a number of compounds, particularly for hydrocarbons, their halogen and oxygen derivatives, is a rather exact additive quantity and may be regarded as a sum of atomic refractions.

Atomic refractions can be calculated in the following way: from the experimentally found values of molar refractions the mean difference of R per CH_2 (the homologous difference) is determined for the members of a homologous series. If from the value of R, say, for hexane, C_6H_{14}, we subtract six values of R per CH_2, we will obtain the value for two hydrogens:

$$R_{C_6H_{14}} - 6R_{CH_2} = R_{2H}$$

Having divided in half, we obtain the atomic refraction of a hydrogen atom, A_H. Evidently, the atomic refraction of the carbon atom, A_C, will be:

$$A_C = \frac{R_{C_6H_{14}} - 14A_H}{6}$$

From the value of R, say, for $CH_3—CH_2OH$, we can find the atomic refraction of the alcoholic oxygen, A_O, if the atomic refraction of five carbon atoms ($5A_C$) and six hydrogen atoms ($6A_H$), etc., is subtracted from $R_{C_2H_5OH}$.

For the oxygen atom, the value of atomic refraction may, however, be different, depending on its function; just as for the carbon atom, depending on whether it is saturated (tetrahedral), olefinic or acetylenic. But in calculations of atomic refractions it is preferred to regard A_C as a constant quantity and to introduce a correction (an extra increment) for a double or triple bond.

The atomic refractions of the elements and the increments for the multiple C=C and C≡C bonds for the sodium D line are as follows:

C	2.418	N (in NH_2)	2.322
H	1.100	N (in NHR, fatty)	2.499
O (in OH)	1.525	N (in NR_2, fatty)	2.840
O (in ethers and esters)	1.643	Increment for C=C	1.733
O (carbonyl)	2.211	C≡C	2.398
Cl	5.967	C / \ C	
Br	8.865		
I	13.900		0.6

Systematic studies of molar refractions have been carried out by Brühl, Eisenlohr and Auwers. Molar refraction was the first physical constant widely used in organic chemistry for the deduction of the

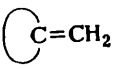
structure of organic molecules. Unfortunately, the area of its application is restricted to hydrocarbons, their halogen and oxygen derivatives since the constancy of atomic refractions is not great for other elements. There is a second essential limitation—the method is applicable only to liquid substances. The molar refractions of solid substances can be determined in solutions by the difference, but this is much less accurate since this difference takes on all the errors.

The first and most widespread application of molecular refraction in organic chemistry is in the field of analysis. If, for example, n_D^{20} and d_4^{20} have been determined, we can calculate R for a substance with a known molecular weight. On the other hand, on the basis of the suspected structural formula we can calculate the value of R from the atomic refractions and the extra increments for double and triple bonds. For a pure substance the coincidence of the value found experimentally with that calculated lies usually within the limits of 0.1-0.2 and often amounts to 0.02. The correctness of the suspected formula is judged by this coincidence. Of course, isomers cannot be differentiated in this way if they do not differ functionally, or by the presence or absence of multiple bonds, or else by the number of multiple bonds.

The character of branching in saturated hydrocarbons, however, affects the value of R, and in the case of highly branched alkanes the value of R is lower than that calculated: for example, by a factor of 0.24 for $C(CH_3)_4$; 0.42 for $(C_2H_5)_3CH$; 0.37 for $(CH_3)_3C—CH(CH_3)_2$. Such deviations of R (just as the exaltation considered below) make it possible to judge about molecular structure; but ordinarily R serves as an independent means to support the analytical data, which of course is also important.

The most valuable applications of molecular refraction are associated with the deviations of this quantity from additivity (with so-called **exaltations**) if there are certain structural peculiarities. For example, the conjugation of two bonds in an open chain gives an increment (exaltation) of R amounting to 2.0 against the calculated value. But the presence, in a system of conjugated bonds, of methyl groups at the second or third carbon atom (and the more so at both) reduces the exaltation to 1.0 (in the case of two CH_3 groups) and even to 0.75. For instance, the exaltation of isoprene is reduced to 1.0, and that of 2,3-dimethylbutadiene to 0.75, while the exaltation for butadiene is normal. The conjugation of $CH_2=CH$ with the benzene ring (styrene) gives an exaltation of 1.3, which decreases for α-methylstyrene and increases (up to 1.4) for β-methylstyrene. Benzene and cyclohexadiene show a value of R almost equal to that calculated (without exaltation); the value is even lower for benzene. But, in general, the conjugated position of double bonds in rings gives a slight increase of R; for example, cyclooctotetraene has an exaltation of 0.33 and cyclooctatriene, 0.66. A very characteristic exaltation is

shown by the so-called semicyclic double bond, i.e., by a structure of the type



The exaltation in this case is 0.3. The conjugation of C=C with C=O also gives an exaltation of about 1.0.

(E) Diffraction Methods of Analysis*

An atom is capable of scattering the incident radiation. Light rays, electron or neutron beams, X-rays—all the known types of radiation—falling onto an atom are scattered by it. The rays scattered by individual atoms reinforce or weaken one another, depending on the mutual arrangement of atoms. This phenomenon is known as the **diffraction** of radiation from atoms. It is clear that the diffraction can provide information about the structure of a substance. By determining the direction and intensity of scattered rays it is possible to obtain valuable information about the structure of a molecule, primarily its geometry, i.e., the mutual arrangement of the centres of the atoms. The most efficient method providing information on the geometry of molecules is **X-ray diffraction analysis** of crystals of organic compounds.

A crystalline body, in contrast to an amorphous one, has a well-defined external form (faces) well visible in the rays of ordinary light, and also a clear-cut three-dimensional periodicity of the internal (atomic) structure, which is revealed only by the scattering of X-rays and neutron or electron beams. In other words, the three-dimensional periodicity means that the crystal can be regarded as an assembly of identical parallelepipeds (a space lattice): one parallelepiped when moved parallel to itself will fill all the crystalline space and in such a way that the vertices of this parallelepiped will be found at identical points. Such a parallelepiped which can be repeated to form the entire crystal lattice is called the **unit cell**, and the sizes of the three edges are equal to the **identity periods** of the crystal.

Such a clear-cut three-dimensional periodicity in the arrangement of the particles of a substance (atoms or molecules) gives rise to diffraction effects on scattering of X-rays: in some directions the rays reinforce each other, and in others they cancel each other. A system of spots—**reflections**—appear on a photographic film (an X-ray diffraction pattern). These reflections differ from each other by the extent of photographic blackening.

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* This section was written by A.I. Kitaigorodsky.

The principal law that governs the geometry of a diffraction pattern was enunciated by the English physicists W. H. Bragg and his son W. L. Bragg and the Russian crystallographer G. V. Wulff. It has been found that the direction in which all the waves reinforce each other is accounted for clearly and simply as follows: an intense ray is, as it were, reflected by a plane passing through all the lattice points. All the nodal planes of the crystal lattice project in parallel families. To each of these families there corresponds a certain definite interplanar spacing denoted usually by the letter d. The "reflection" of the ray by a system of planes occurs not at any angle of incidence but only when the radiation wavelength λ, the angle of diffraction θ and the interplanar distance d are interrelated by the formula

$$2d \sin \theta = n\lambda$$

where n is a whole number.

By using this law one can set up a system of rules, with the aid of which, on the basis of the diffraction pattern geometry, the lattice geometry can be fully characterized, i.e., the symmetry and unit-cell dimensions of the crystal can be determined. It is possible to relieve the investigator of the burden of such calculations by using the ingenious photographing methods. In one method (called the rotating-crystal or moving-film technique), the rotation of the crystal is coupled to a to-and-fro movement of the film, parallel to the axis of rotation of the crystal, a special screen with a narrow slit being placed between the film and the crystal. Such methods make it possible, in a certain sense, to photograph the crystal lattice. Figure 3.2 shows an X-ray diffraction pattern. The black spots are seen to be within a rectangular net, the unit cell of which reflects the corresponding section of the unit cell of the crystal. Owing to the specific feature of diffraction the pattern obtained is "reverse"—the distances between the spots are proportional not to the repeating periods in the crystal lattice but to their reciprocal values.

X-rays are scattered from electrons (electron beams are scattered from electrons and atomic nuclei; neutron beams are scattered from nuclei). The X-ray method allows us to locate the "electron centre" of the atom. Evidently, the mean position of the nucleus is but slightly shifted relative to the "electron centre" of the atom.

To conduct a complete X-ray experiment, a crystal is needed, whose linear dimensions do not exceed 1 mm. Optical (by the reflection of the light ray from the external faces) and X-ray orientations of the crystal in the X-ray chamber are possible.

There exist the various types of X-ray chambers, which permit photographing a fixed (immobile) or rotating crystal, with the film being fixed or moved synchronously with it. The valuable diffraction patterns obtained by any photographing method are used at two stages of X-ray analysis.

First stage. *Geometric measurements.* The distances between the reflections and sometimes also the angles allow us to calculate the volume of the unit cell, V, after which it is easy to determine the molecular weight of the substance, M, if its density ρ is known:

$$M = \frac{\rho V}{gZ}$$

where $g = 1.67 \times 10^{-24}$ g is the mass of the hydrogen atom and Z is the number of molecules in the unit cell.

In studying the geometry of the diffraction pattern it is not difficult to reveal definite regularities in the cancelling of a family of

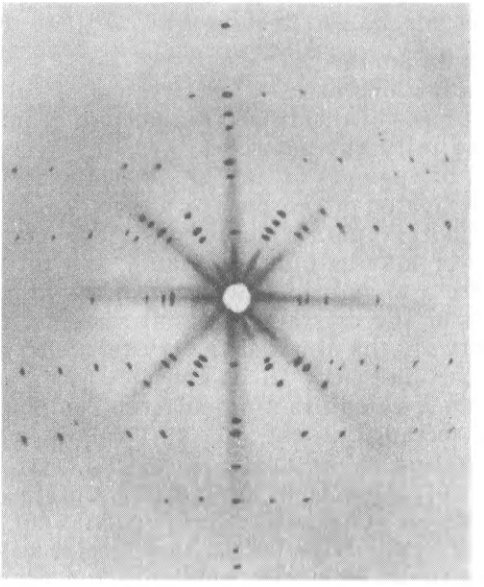


Fig. 3.2.
X-ray photograph of a molecular compound of aniline with trinitrobenzene.

reflections, from which one can nearly always determine unequivocally the symmetry of the crystal under study. The symmetry imposes limitations on the value of Z, which of course cannot be a fractional number, but for organic crystals most often Z takes on the values 1, 2, 4 or 8.

Not infrequently the symmetry of a crystal determines unequivocally not only Z but, as a consequence, the symmetry of the molecule in the crystal as well. Guided by the principal idea of organic crystallochemistry (A. I. Kitaigorodsky) —the idea of close packing

of molecules in a crystal, i.e., such a packing of molecules in which the "hills" of one molecule fit into the "valleys" of the other, we cannot infrequently choose a single structure for a given molecule among a series of structural models.

Second stage. *Estimation of reflection intensities on X-ray photographs and their mathematical treatment.* This stage is much more time-consuming than the first one. But it gives the values of all the interatomic distances (with an accuracy of 0.01 Å) and all the valency angles (with an accuracy of 0.5°) in the molecule of the substance under study.

The intensity of each scattered ray is associated with the structure of the crystal. Suppose the unit cell of a crystal (let us assume, for simplicity, that the crystal is centrosymmetric) contains N atoms with the coordinates $x_1y_1z_1$, $x_2y_2z_2$, ... Then let h, k, and l designate the interference indices, which are used for numbering the reflected rays. As known from crystallography, each nodal plane in the crystal lattice is described with the aid of three integral Miller indices h', k', l'. The interference indices are related to the Miller indices as follows:

$$h = nh'; \quad k = nk'; \quad l = nl'$$

It can be shown that the amplitude F of the wave of a diffracted ray with the indices h, k, l may be represented by the formula

$$F_{hkl} = 2 \sum_{j=1}^{N/2} f_j \cos 2\pi (hx_j + ky_j + lz_j) \qquad (1)$$

Here the summation is carried out over all the atoms contained in the unit cell. The quantity f_j represents the scattering of the wave by one atom. The values of atomic amplitudes for all the elements are tabulated and can be found in special publications.

It should be noted that experiment provides the value of ray intensity, and the intensity is proportional to the square of the amplitude. Thus, if the structure is known, then the amplitude of the scattered ray and its intensity can be calculated unequivocally. But, unfortunately, the chemist is more interested in the converse problem—the deduction of the structure from the known intensities. Since it is impossible to find out, by experiment, whether the amplitude is positive or negative, this problem cannot be solved directly. It may be said that the main task of the investigator in the field of crystal-structure analysis is the application of the various kinds of techniques, with the aid of which the sign of the amplitude can be determined.

It is quite possible that the further development of computing technique will allow us to deal only with the solution of the direct problem. With the enormous number of operations per second the computer is able to calculate the intensity pattern from millions of the various "trial" structures. These calculations must be compared

with experimental data. Of these "trial" structures the one for which the calculated amplitudes coincide with those measured will be correct.

In spite of the immensity of such a task (one to three thousands of diffracted rays are measured and the results obtained are matched against the experimental data for each "trial" structure), it is undoubtedly feasible even for very complex structures. The point is that it is not required that all the possible structures be tried. As a rule, before the analysis is started the investigator has at his disposal the preliminary data on the chemical formula, and the distances between the covalently bonded atoms are also known beforehand with a sufficient accuracy. Finally, by using the principle of closest packing we may discard all the mutual dispositions of molecules that are not in agreement with this rule. Thus, having set up a program of operations we can start a sufficiently reliable search for the correct structure. Highly complicated structural problems have been solved by using the mathematical method, the so-called method of "valleys", developed in this country by I. M. Gel'fand.

But so far the solution of a structural problem is accomplished in a different way. The work begins with the "guessing" of the signs of structure amplitudes. The signs can be determined at the very outset if at least an approximate structural model is available. This approximate model is obtained by calculation of a Fourier series, whose coefficients are the experimentally measured intensities of diffracted rays. Here we mean the Patterson series or the series of interatomic vectors. This three-dimensional function can be represented by the following formula:

$$A(u, v, w) = \sum F_{hkl}^2 \cos 2\pi (hu + kv + lw) \qquad (2)$$

The summation is usually taken over a million points in the unit cell by dividing each of the unit-cell edges into a hundred parts and the sum consists of one to three thousands of terms. It is quite clear that such an amount of calculations can only be performed with the aid of electronic computers. In this case, the problem is solved rapidly and, as shown by Patterson, series of this kind make it possible to construct an approximate structural model owing to their remarkable property: the peaks in the Patterson three-dimensional function give the coordinates of the vector distances between pairs of atoms, which exist in the real structure, the heights of these peaks being proportional to the product of the atomic numbers of the atoms concerned. Owing to this property the interatomic vectors connecting the heavy atoms are sharply prominent in the Patterson series.

Structures containing heavy atoms are especially convenient for investigations. The point is that in calculations of the signs of structure amplitudes on the basis of formula (1) we can, at a first approximation, neglect the contribution of the light atoms to the sum.

This being done, the procedure of structure elucidation consists of the following steps. *The first step*: the coordinates of the heavy atoms are determined from the Patterson series. *The second step*: the signs of all the structure amplitudes are determined from formula (1). *The third step*: an electron-density series is set up:

$$\rho(x, y, z) = \sum F_{hkl} \cos 2\pi (hx + ky + lz)$$

This formula closely resembles formula (2) but there is an essential difference between them. The cosine factors are not the squares of the measured structure amplitudes but the amplitudes themselves. They are substituted into this formula with signs found from the coordinates of the heavy atoms.

The computation at about a million points enables an electron-density distribution to be derived for any cross-sectional area of

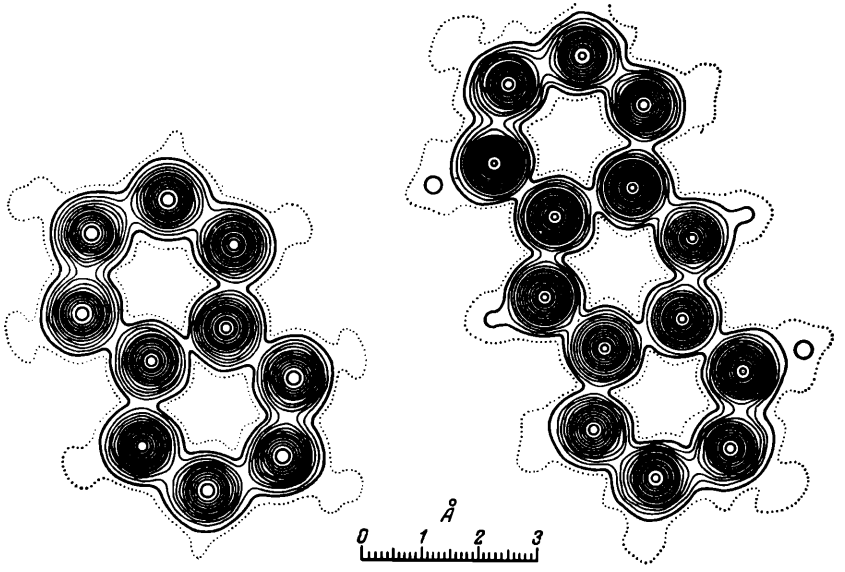


Fig. 3.3.

Electron-density contour maps of naphthalene (left) and anthracene (right).

the unit cell. To illustrate, Fig. 3.3 shows the electron-density maps for crystals of naphthalene and anthracene. The lines drawn are contours of equal electron density. The apexes of the electron hills are interpreted as the centres of the atoms.

If the result obtained is controversial, one has to resort to a series of successive approximations, namely, the signs of the structure amplitudes are again calculated, this time for a new model which has

been revealed by the first electron-density map. A second, better pattern of the structure is obtained. Normally, the third calculation is the final one. All calculations are performed on electronic computers.

As seen, a complete structure determination is rather complicated. For this reason an investigation of this kind is far from being justifiable in every case.

The physical investigations so far carried out (chiefly, X-ray studies) permit us to reliably construct *a priori* the models of organic molecules. This model construction is based on the fact that every atom can roughly be characterized by two "radii", the values of which are independent of the molecule containing the atom. The distances between the covalently bonded atoms are considerably smaller than those between the atoms belonging to different molecules.

One half of the bond length, i.e., the distance between two identical atoms joined by a covalent bond, is called the **atomic radius.** The halfway distance of nearest approach of two like atoms of two adjacent molecules is called the **intermolecular radius** (or the van der Waals radius). Table 3.9 lists the values of these quantities.

TABLE 3.9. **Atomic and Intermolecular (van der Waals) Radii of the Elements**

Element	Atomic radius, Å	Intermolecular radius, Å	Element	Atomic radius, Å	Intermolecular radius, Å
H	0.30	1.17	F	0.64	1.35
B—	0.88	1.76	P—	1.10	1.9
B=	0.76	1.76	P=	1.00	1.9
B≡	0.68	1.76	P≡	0.93	1.9
C—	0.771	1.8 (1.72*)	S—	1.04	1.85
C=	0.665	Ditto	S=	0.94	1.85
C≡	0.602		Cl	0.99	1.80
N—	0.70	1.57	As—	1.21	2.00
N=	0.60	1.57	Se—	1.17	2.00
N≡	0.55	1.57	Br	1.14	1.95
O—	0.66	1.38	I	1.33	2.10
O=	0.55				

* In large aromatic molecules.

(In order to obtain the bond length, the corresponding atomic radii must be added up. This may be illustrated by some examples: 1.542 Å for C—C; 1.33 Å for C=C; 1.215 Å for C=O.)

The methods of X-ray analysis enable us to locate the centres of atoms. If spheres are drawn from these centres with the aid of the corresponding intermolecular radii, the external surface of the intersecting spheres will define the shape and volume of the molecule. The packing of such spatially defined molecules obeys the principal rule of organic crystallochemistry.

In practice, in order to construct the model of a molecule, a set of spheres (drawn to a certain scale, say, 1 Å = 1 cm) with sections is

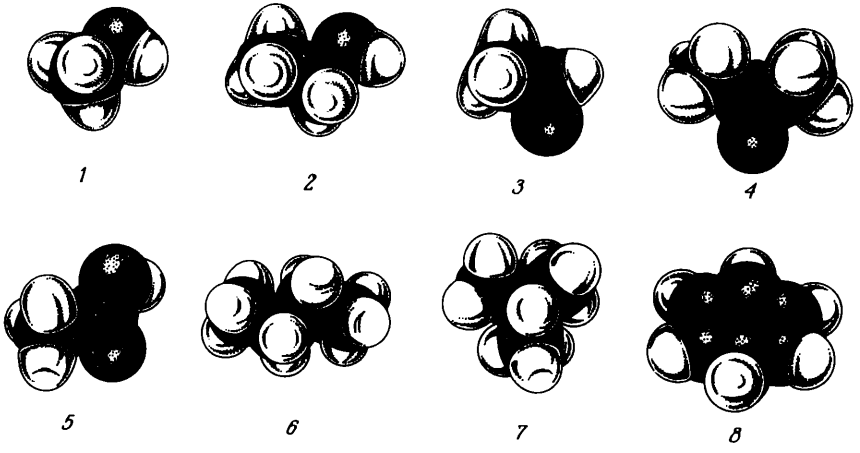


Fig. 3.4.

Stuart-Briegleb molecular models:

1 – methyl alcohol (methanol); 2 – ethyl alcohol (ethanol); 3 – acetaldehyde; 4 – acetone; 5 – acetic acid; 6 – butane; 7 – isobutane; 8 – benzene.

required. The number of sections on each sphere is equal to the number of atoms linked to a given atom by a covalent bond. The planes of the sections are perpendicular to the valency directions, and the distances from these planes to the centre of the sphere are equal to the corresponding atomic radius; the radii of the spheres are equal to the intermolecular radii. Figure 3.4 shows some molecular models.

The X-ray studies of organic compounds have provided a direct confirmation of the principal rules of stereochemistry. Among the first results obtained by X-ray analysis were those for the crystal structures of diamond and graphite.

In the structure of diamond (Fig. 3.5), the distance between two neighbouring carbon atoms is 1.54 Å. Proceeding from the idea of the tetrahedral linkage of the tetravalent carbon atom, it appears that all the carbon atoms in diamond are bonded covalently, i.e., the whole crystal is one vast structure. In order to crush a piece of diamond, it is necessary to overcome the forces of chemical bonds, which accounts for the extraordinary strength of diamond.

In the structure of graphite, the carbon atoms are arranged in layers, each atom closely bound to three others in the same plane so that the structure looks like a vast sheet of little hexagons (Fig. 3.6). The distance between neighbouring atoms in the sheets is 1.41 Å. The sheets of atoms are separated by 3.35 Å, i. e., the distance is only slightly lower than the sum of the intermolecular C—C radii. Hence, in graphite, each plane is a molecule, consisting of aromatic carbon hexagons. The weak bond between the planes is responsible

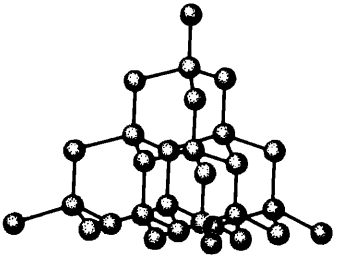


Fig. 3.5.
The crystal lattice of diamond.

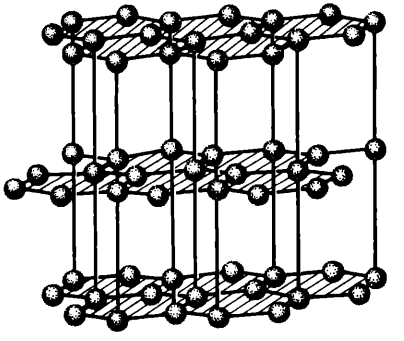


Fig. 3.6.
The crystal lattice of graphite.

for the complete cleavage and platelike structure of graphite perpendicular to this bond.

These results have been conclusively verified by studies of the structures of symmetrical organic molecules: all molecules of the CR_4 type have tetrahedral valence angles, and benzene and its hexaderivatives have angles equal to 120° and a flat structure. Deviations of valence angles from these "normal" values have been observed and thoroughly studied. They arise in nonsymmetrical substitution reactions as a result of so-called spatial interactions (the interactions between the non-bonded atoms of the same molecule). It has been found that if in a molecule the distances between the atoms are considerably smaller than the sum of intermolecular radii, a spatial interaction takes place between these atoms, which leads to the distortion of the normal valence angles or hinders the free rotation about the bonds. The strains existing in cyclic systems are partly accounted for by the approach of non-bonded atoms to distances smaller than the sum of intermolecular radii.

It is obvious in connection with what has been said above that X-ray diffraction analysis should be resorted to in the following cases: first, when the structure of a chemical compound has not been

completely elucidated; second, when the stereochemistry of the molecule is obscure; third, when the exact values of interatomic distances are to be determined since the atomic radii given above are average values.

This task is of relatively little interest because the interatomic distances serve only as a crude characteristic of the chemical properties of the bond and the accuracy of their determination is comparatively low. As an example, the distance between an aromatic carbon atom and a chlorine atom linked to it coincides, within the limits of measurement accuracy, with the distances between an aliphatic carbon atom and chlorine. At the same time, a number of properties of these bonds (for example, the dipole moment, the frequencies of valence vibrations) are prominently different for the two cases.

Diffraction methods have no competitors as far as determination of the spatial arrangement of atoms is concerned. X-ray methods are the most important in this respect, but *neutron diffraction* also plays an important role. The hydrogen atom scatters X-rays very weakly, and the accurate location of hydrogen atoms in a structure by the X-ray method is difficult and is usually not even attempted. The neutron diffraction of organic compounds is of great value because it provides an answer to this problem—it enables hydrogen atoms in a crystal structure to be accurately located.

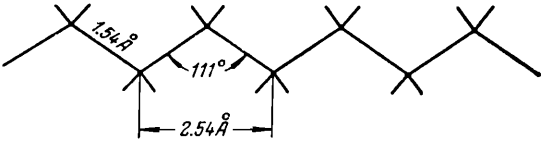
As regards *electron diffraction*, this method has a number of advantages only in the investigation of gases and vapours. The diffraction by gases and vapours, however, provides much less information on structure than the diffraction by crystals. The structures of simple molecules are largely known; in more complicated cases the use of electron diffraction is not expedient. Electron diffraction is useful in determinations of the distances between heavy atoms and atoms of organogenetic elements. Therefore this method continues to be of value in the study of organometallic compounds.

The experimental and theoretical methods of X-ray diffraction analysis have been brought to a high level of perfection in recent years. There is practically no limitations as regards the complexity of molecules in the determination of the spatial arrangement of their atoms (it will suffice to mention vitamin B_{12} and the protein myoglobin). The success depends on the amount of work and the availability of a small single crystal of the substance to be studied.

The importance of X-ray diffraction analysis in organic chemistry is not restricted to the possibility of determination of the structure of a molecule. The mutual arrangement of molecules (packing) in a crystal appears to be important to numerous problems. As an example, let us consider the results of the investigation of crystals built up of long-chain molecules.

Paraffins, fatty acids and other long-chain compounds are characterized by a planar zig-zag structure consisting of CH_2 groups. Be-

cause of the tetrahedral angle between the bonds, with the length of the C—C bond being 1.54 Å, the carbon atoms are arranged in repeating patterns every 2.54 Å along a straight line which is the axis of the zig-zag line:



The ideal tetrahedral angle of 109°28′ increases in this molecule by about 2° due to the repulsion of the non-bonded carbon atoms.

X-ray studies have demonstrated that when the molecule increases by $n$$CH_2$ groups, one of the identity periods increases by $n \times$ $\times$ 2.54 Å, while the other two dimensions of the unit cell remain practically unchanged. Hence, the long axes of molecules lie in a parallel fashion in a crystal.

In a section perpendicular to the long side of the unit cell, the packing depends on the disposition of side groups. In paraffins, two neighbouring molecules are shifted relative to each other along the long axis so that the hydrogen atoms of the CH_2 group of one molecule are found to be in the "valley" between the two CH_2 groups of the neighbouring molecule, i.e., by one half of 2.54 Å.

In fatty acids, the carboxyl groups of two adjacent molecules are turned to each other and thus form stable hydrogen bonds, and the methyl groups touch the methyl groups of two other molecules; in this case the bond is weak. It is understandable why fats, like graphite, are good lubricants.

X-ray diffraction analysis can be applied most successfully to substances forming single crystals. The study of polymers, however, also yields interesting results. A number of important properties of high-molecular-weight compounds, in which the long-chain molecules are arranged with a high degree of ordering, have been elucidated only with the aid of the X-ray method.

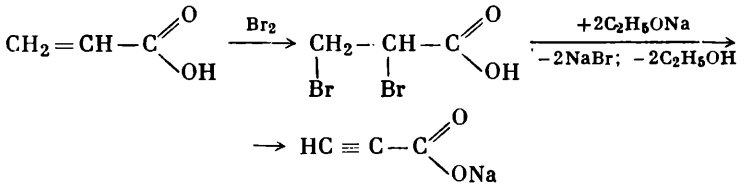
The nature of natural rubber, cellulose, synthetic polymers, protein molecules could not have been clarified without the application of X-ray diffraction analysis.

The physical methods of investigation of organic compounds will also be considered in Volume II.

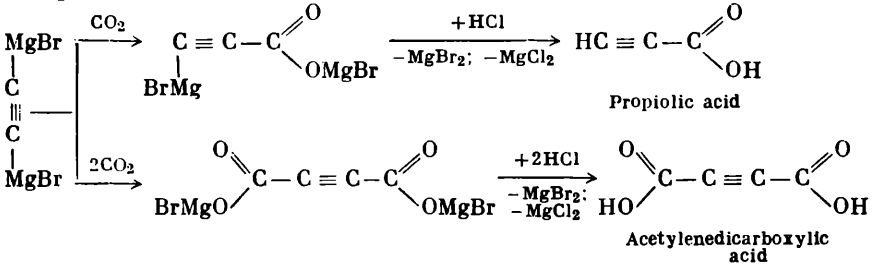
D. Carboxylic Acids of the Acetylene Series

Apart from the ordinary methods of preparation of the acids of the acetylene series from the corresponding ethylenic acids, for exam-

ple,



the acetylene carboxylic acids with the adjacent position of the carboxyl group and acetylenic carbon atom can be obtained from Iotsich compounds:



In this way, from propyne there is prepared tetrolic acid, CH_3—$-C{\equiv}C-COOH$.

The physical properties and names of the acetylene carboxylic acids are listed in Table 3.10.

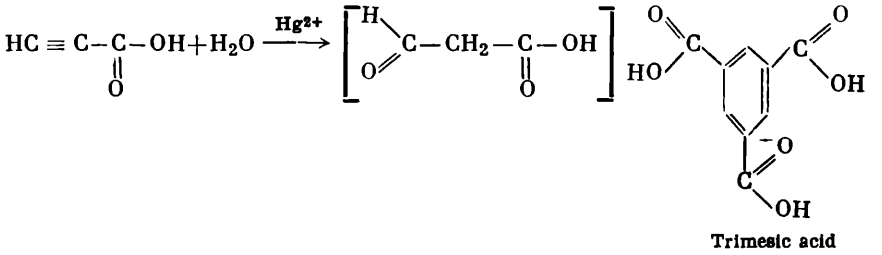
TABLE 3.10. **Acids of the Acetylenic Series**

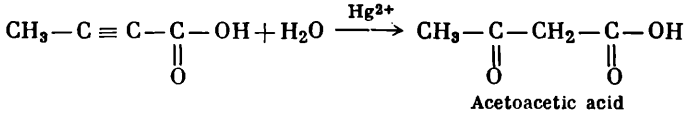
Formula	Name	m.p., °C	b.p., °C
$HC \equiv C-COOH$	Propiolic or propargylic*	9	144 (dec.)
$CH_3-C \equiv C-COOH$	Tetrolic or methylpropiolic	76.5	203
$C_2H_5-C \equiv C-COOH$	Ethylpropiolic	50	—
$C_3H_7-C \equiv C-COOH$	Propylpropiolic	27	127 (at 24 mm Hg)
$HOOC-C \equiv C-COOH$	Acetylenedicarboxylic	179	—

* The density of the acid (d_{15}^{15}) is 1.139.

Acetylenic acids possess an increased acidity as compared with saturated acids. They are capable of adding two or four hydrogen

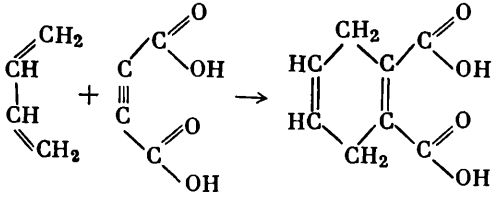
atoms (over Fe, Pd, or Ni); two molecules of halogen (Cl_2, Br_2, I_2) or of hydrogen halide; and a molecule of water in the presence of mercuric ion:





Naturally, the acetylenic hydrogen atom of propiolic acid is capable of being replaced by Ag, Cu(I).

Like maleic acid and its anhydride, acetylenedicarboxylic acid is a dienophile (see page 369):



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Academician ALEKSANDR NIKOLAEVICH NESMEYANOV was one of the most distinguished organic chemists of our time. He conducted fundamental research in the field of organoelement chemistry and authored important and original works on organic and theoretical chemistry. The concept of organoelement (elemento-organic) chemistry was introduced by A.N. Nesmeyanov. He devised diazo method of synthesis of organometallic compounds, discovered new classes of compounds, demonstrated relationship between structure and reactivity of metallic derivatives of tautomeric systems. His principal areas of interest were the chemistry of organometallic compounds and general problems of organic chemistry. Nesmeyanov initiated and directed a number of new trends of investigation, one of which was the preparation of synthetic and artificial food. Among the practical achievements in the investigations carried out by Nesmeyanov and his school may be mentioned the development of valuable medicinal preparations, the synthesis of a new antiknock compound and the preparation of a number of materials for special technical applications.
Nesmeyanov was awarded the State Prize for his investigations in the field of organoelement compounds and the Lenin Prize for his remarkable contributions to the development of the science and practical implementation of the scientific achievements in the national economy.
A. Nesmeyanov was an honorary member of the Royal Society (Great Britain), and of academies of science of many countries, including the New York Academy of Sciences (USA).
A.N. Nesmeyanov died in 1980.

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